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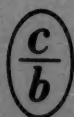
# **DOKLADY CHEMISTRY**

PROCEEDINGS of the  
ACADEMY OF SCIENCES  
of the USSR

Chemistry Section

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(DOKLADY AKADEMII NAUK SSSR)

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# THE STRUCTURE OF MOLECULES AND THE KINETICS OF THEIR CATALYTIC HYDROGENATION

Academician A. A. Baiandin and M. L. Khidekel\*

The effect of substituents at atoms undergoing catalytic hydrogenation on the rate,  $\underline{v}$ , of the reaction has been studied repeatedly. Such effect can be due both to steric and to energetic factors, and these factors are interconnected. In the present work, the case in which the energy factors predominate is given the major consideration.

A number of authors [1-3] have pointed out the existence of a parallel between  $\underline{v}$  and the heat of hydrogenation,  $\underline{u}$  (or values connected with it). However, in the hydrogenation of benzene and a number of its methyl derivatives,  $\underline{v}$  decreases with an increase in the number of substituents when the hydrogenation is carried out over Ni catalyst [4], and increases when the catalyst is  $WS_2$  [5], the order in which  $\underline{u}$  changes remaining constant. Similarly, the decrease in  $\underline{v}$  has sometimes been explained by the presence of energy of conjugation,  $\sigma$  [6, 7], although in other cases (more rarely) conjugation is accompanied by an increase in  $\underline{v}$  [8, 9].

It has been proposed that  $\sigma$  is completely lost during adsorption [10-12], but the reason for the decrease in  $\underline{v}$  in such cases was not indicated. An effect of  $\sigma$  on the observed activation energy,  $\epsilon^*$ , has not been detected [13].

According to the multiplet theory [14],  $\underline{v}$  decreases with a decrease in the heat of formation,  $E$ , of the intermediate multiplet complex, since  $\epsilon^* \approx -0.75E$ , where  $\epsilon^*$  is the true activation energy. For hydrogenation of an unsaturated compound, in particular, an olefinic bond [15]:

$$E = -Q_{C-C} - Q_{H-H} + Q_{C-K} + Q_{C-K} + 2Q_{H-K} - r\sigma, \quad (1)$$

$$u = -Q_{C-C} - Q_{H-H} + Q_{C-H} + Q_{C-H} - \sigma. \quad (2)$$

Here,  $Q$  represents energies of reacting bonds;  $K$  is the catalyst;  $\sigma$  is the energy of conjugation (stabilization), which is connected with delocalization of electrons and which changes during the reaction, the value of  $\sigma$  being dependent on the structure of the molecule;  $r \approx 1/2$  is the fraction of  $\sigma$  lost by the hydrogenatable substance during catalytic adsorption. According to Equations (1) and (2), a change in the nature of a substituent at  $C_1$  has an effect on  $E$  and  $u$ :

$$\delta E = -\delta Q_{C-C} + \delta Q_{C-K} - r\delta\sigma, \quad (3)$$

$$\delta u = -\delta Q_{C-C} + \delta Q_{C-H} - \delta\sigma. \quad (4)$$

Here,  $\delta Q_{C-C} = C$ ,  $\delta Q_{C-K}$ ,  $\delta Q_{C-H}$  are changes in the inductive and hyperconjugative effects, and  $\delta\sigma$  is the conjugation energy involved in the substitution.

It follows from Equations (3) and (4) that substitution: 1) does not change  $\underline{v}$  if  $\delta Q_{C-C} = C = \delta Q_{C-K}$  and  $\delta\sigma = 0$ ; 2) can cause an increase in  $\underline{v}$  with an increase in  $\underline{u}$  (if the increase in  $\delta Q_{C-K}$  parallels the increase in  $\delta Q_{C-H}$ ; i.e., if the induction and hyperconjugation effects act in the same direction on  $C_1$ , which bonds both to  $K$  and to  $H$ ), or can cause a decrease in  $\underline{v}$  in the contrary case (see above [4, 5]); 3) can decrease the reaction rate in the presence of a conjugation energy, particularly in the case where  $\sigma$  changes considerably ( $r\delta\sigma \gg \delta Q_{C-K} - \delta Q_{C-C}$ ); 4) can cause an increase in  $\underline{v}$  when  $\sigma$  is small and the energy of the bond with the catalyst increases under the influence of induction and hyperconjugation effects, i.e.,  $|\delta Q_{C-K}| > r\delta\sigma + \delta Q_{C-C}$ .



TABLE 1

Hydrogenation over Rh Catalyst. Solvent  $C_2H_5OH + NaOH(0.0018\%)$ , Catalyst No. 5

Compound	$\sigma$ , kcal/mole	$k_{1/2}$ , ml/min	Temperature interval, °C	$\epsilon$ , kcal/mole
Benzene	36,0[18]•	3,3	2-20	3,7
Pyridine	42,2[20]•	3,3	2-20	6,3
Pyrrole	24 [21]•	3,2	10-30	7,0
Furan	17,2[18]	14,1	0,6-10	3,4

• From the heat of hydrogenation.

•• From the heat of combustion.

decrease in the volume of hydrogen (STB) after 15, 30, and 60 seconds. The substances studied had constants in agreement with those in the literature. All of the data relate to 1 g of catalyst. When necessary the potential of the catalyst was measured [17].

TABLE 2

Hydrogenation over Rh Catalyst (A and C, solvent  $CH_3COOH$ ; Catalysts Nos. 6 and 7; B, D, E, F, and G, solvent  $C_2H_5OH$ ; Catalysts Nos. 9, 8, 10, 6, 7, respectively)

Compound	$\sigma$ , kcal/mole	$k_{1/2}$ , ml/min	Temperature interval, °C	$\epsilon$ , kcal/mole
A. Benzene	36,0	3,6	15-30	7,2
1,3-Cyclohexadiene	1,8[18]••	4,0••••	15-30	8,6
1,4-Cyclohexadiene	0	44,2	15-40	2,8
B. Furan	17,2	25,4	5-20	4,4
3,4-Dihydrofuran	0	95,7	5-20	5,7
C. Ferrocene	113,0[19]•••	0,3	—	—
Benzene	36,0	10,2	—	—
D. Ethylcyclopropane•	—	0,0	—	—
Phenylcyclopropane•	—	4,4	—	—
E. Eugenol	—	62,0	2-30	4,9
cis-Isoeugenol	2	50,7	2-30	6,0
trans-Isoeugenol	—	37,0	—	—
F. Cyclopentadiene	2,9[18]••	36,4	5-30	4,8
Cyclopentene	0	40,5	5-30	3,6
G. Benzene	36,0	8,8	—	—
Cyclopentadiene	2,9[18]••	92,0	—	—

• These preparations were kindly given to us by B. A. Kazanskii, M. In. Lukina, I. L. Sofonova and S. V. Zotova.

•• From the heat of hydrogenation.

••• From the heat of combustion.

•••• As in original - Publisher's note.

We studied the kinetics of the hydrogenation of benzene (B), pyridine (P), pyrrole, furan (F), some of their derivatives, 1,4-cyclohexadiene (1,4-CHD), 1,3-cyclohexadiene (1,3-CHD), 3,4-dihydrofuran (DHF), cyclopentadiene (CPD), cyclopentene (CP), eugenol (E), and cis- and trans-eugenol (CE). The order of the reaction, which was determined from the change in concentration over wide limits, was zero for all compounds. The rate changed in proportion to the amount of catalyst.

Below are presented the results of a systematic investigation of the kinetics of hydrogenation of typical representatives of compounds with aromatic and conjugated bonds (in particular, bonds differing with respect to  $\sigma$ ); the purpose of the investigation was to study the effect of  $\sigma$  on  $v$ .

The hydrogenation was carried out at temperature of 5-60° in a thermostatted, rapidly rocking bomb at atmospheric pressure. The catalyst was rhodium on aluminum oxide (0.08-2.5%). The low-rhodium-content catalyst was prepared by a method developed by us. Rhodium was selected owing to its high activity and to its ability to promote the hydrogenation of aromatic compounds under mild conditions with a minimum of side reactions, which became known recently [16]. The reaction rate was measured by the



TABLE 3

Hydrogenation over Rh Catalyst (A, B, and C, 20°; D, 15°;

A) solvent, CH<sub>3</sub>COOH, Catalyst No. 1; B, C, and D) solvent, C<sub>2</sub>H<sub>5</sub>OH, Catalyst Nos. 2, 3, and 4)

Compound	$\sigma$ , kcal/mole	$\rho^*$	Compound	$\sigma$ , kcal/mole	$\rho$
A. Benzene	36,0	1,000	C. Pyridine	42,2	1,000
Ethylbenzene	35,2[18]**	0,426	$\alpha$ -Picoline	48,5[20]***	0,519
Cumene		0,407	$\beta$ -Picoline	48,2[20]***	0,546
p-Cymene		0,462	$\alpha$ -Ethylpyridine		0,585
Mesitylene	33,1[18]**	0,343	Picolinic acid		0,389
Durene		0,371	$\alpha$ , $\alpha'$ -Bipyridyl		0,078
Benzoic acid	67	0,250	D. Furan	17,2	1,000
Ethyl benzoate	91	0,343	$\alpha$ -Methylfuran		0,961
B. Pyrrole		1,000	$\alpha$ -Ethylfuran		0,952
$\alpha$ -Methylpyrrole	24	0,924	$\alpha$ -n-Propylfuran		0,930
			$\alpha$ -Furancarboxylic acid		0,821

\*  $\rho = k_t$  of the derivative/ $k_t$  of the corresponding aromatic compound.

\*\* From the heat of hydrogenation.

\*\*\* From the heat of combustion.

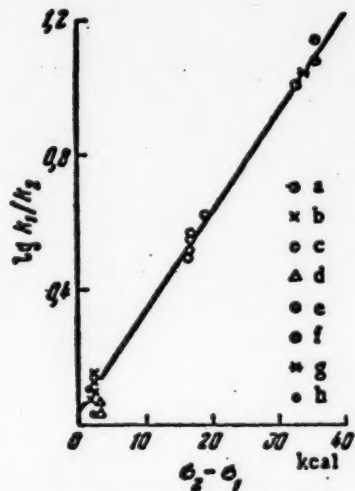


Fig. 1. Dependence of  $\lg k_1/k_2$  and  $\sigma_2 - \sigma_1$ : a) for B and CPD (Table 2, G); b) for E and CE (Table 2, E); c) for F and DHF (Table 2, B); d) for CPD and CP (Table 2, F); e) for B and F (Table 1); f) for B and 1,4-CPD (Table 2, A); g) for B and 1,3-CPD (Table 2, A); h) for 1,3-CPD and 1,4-CPD (Table 2, A)

$\sigma$  for mesitylene (33 kcal/mole [18]) is close to  $\sigma$  for benzene (36 kcal/mole [18]), while the ratio of the rate constants for these compounds is 0,343.

The results of the experiments are presented in Table 1-3; these results permit formulation of the following conclusions (experiments carried out with portions of catalyst of the same catalyst number and with the same solvent are compared):

1. An increase in the conjugation energy of the hydrogenatable compound decreases the rate constant,  $k$ . This was observed both on going from an aromatic compound to a closely similar nonaromatic compound (benzene, 1,4-cyclohexadiene, Table 2, A) and on comparing compounds having different conjugation energies (benzene, furan, Table 1; benzene, cyclopentadiene; benzene, 1,3-cyclohexadiene, Table 2).

2. Conclusion 4, formed above from Equation (3), explains the activation of the cyclopropane ring by the introduction of a phenyl group which conjugates with it (Table 2, D). This phenomenon was also observed and investigated in detail by B. A. Kazanskii and co-workers for the hydrogenation of a number of compounds over Pd and Pt [8, 9]. The activating effect of conjugation can be explained similarly in other cases [22].

3. The effect on the rate constant due to substituents introduced into the aromatic ring (see Table 3) may be explained by the action of inductive and hyperconjugation effects on  $Q_{C_1=C}$ ,  $Q_{CK}$  and  $Q_{CH}$  (Equation (3)) and also by steric factors. For example,

4. A change in the temperature does not cause violation of the rule of Paragraph 1 for compounds with differing  $\sigma$ ; however, with closely similar values of  $\sigma$ , this rule can be violated, and this may be explained by an unequal temperature dependence of the adsorption coefficients of the compounds being compared. For example, it is apparent from Table 2 that 1,3-cyclohexadiene is hydrogenated more slowly than 1,4-cyclohexadiene at 15° and more rapidly at 30°.

5. In conformity with Equation (3), a considerable change in the chemical nature of the bonds being hydrogenated can also lead to violation of the rule of Paragraph 1. For example,  $\eta$  is nearly the same for pyrrole and benzene, although  $\sigma$  for pyrrole is less than for benzene (respectively, 24 [21] and 36.0 [18] kcal./mole). This can be explained by the interaction of the nitrogen atom, which possesses an unshared pair of electrons, with the surface of the Rh. In fact, pyrrole changes the potential of the catalyst toward the cathode ( $\Delta V = 50$  mv), while benzene is hydrogenated at a potential close to that of the reversible hydrogen electrode ( $\Delta V = 0$ ).

6. An analysis of these data and of the results of the work reported in reference [23] shows that in the general case, the effect of the catalyst is not so strong as to change the above-indicated dependence (Paragraph 1) when there is a significant difference in  $\sigma$ .

In addition, if the solvent disrupts the aromatic properties of the compound, then this, in agreement with theory, leads to a sharp change in  $k$ . Thus, during hydrogenation of N-pyridinium cyclopentadienylide in alcoholic medium, where this compound has an aromatic character,  $k = 7.8$  ml/minute, while in acetic acid, where the aromatic character of the compound is lost,  $k = 24.0$  ml/minute [24]\*. For benzene,  $k$  is, respectively, 8.8 and 10.2 ml/minute.

7. It is apparent from Tables 1 and 2 that the conjugation energy has no effect on the activation energy; a similar result was obtained in the case of Pt [13]. This phenomenon can be explained by the fact that, in spite of the zero order of the reaction, the observed activation energies are complex values into which the heat of adsorption enters [25]. Consideration of this question on the basis of the theory will be published separately.

8. The majority of the results in Tables 1 and 2 are satisfactorily described by the relationship  $\lg k_1/k_2 = a(\sigma_1 - \sigma_2) + b$ , which was unknown previously. Here,  $k_1$  and  $k_2$  are the observed hydrogenation rate constants for the two compounds being compared,  $\sigma_1$  and  $\sigma_2$  are their conjugation energies, and  $a$  and  $b$  are constants. Figure 1 presents data confirming this equation. The constant  $a$ , which can be found from the slope of the straight line, is approximately 0.030 kcal.<sup>-1</sup>.

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## ON THE REDUCTION OF NICKEL FERRITE WITH GRAPHITE

V. N. Bogoslovskii, M. G. Zhuravleva and Corresponding Member  
AN SSSR G. I. Chufarov

The mechanism of crystallochemical transformations during the reduction of metal oxides with graphite has been studied in detail for iron oxides [1]. In the reduction of more complex chemical compounds in which atoms of different metals are present in the crystal lattice, the process can be expected to occur in a substantially different manner.

Ferrites — compounds of the type  $Me^{2+}Fe_3^{3+}O_4$  with a spinel structure — merit thorough investigation, since their physical properties make them valuable materials in semiconductor technology. Moreover, in a number of metallurgical industries, processes occur with the formation of ferrites and their subsequent reaction.

The material used in the present investigation was nickel ferrite, which was prepared by sintering an equimolar mixture of the oxides  $Fe_2O_3$  and  $NiO$  in air at  $1200^\circ$  over a period of 30 hours. X-ray analysis of the resulting product showed that it was a pure ferrite with a lattice parameter of  $8.333 (\pm 0.005) \text{ \AA}$ . The reducing agent was graphite from Acheson electrodes, and it was calcined under vacuum at  $100^\circ$  prior to use.

The ferrite was carefully ground with the graphite, and was then subjected to reduction. The amount of graphite was three-fold excess of that theoretically required for complete reduction. The crucible containing the weighed sample was suspended from a McBain quartz spring balance having a sensitivity of 0.001 g. The apparatus was connected with vacuum pumps, and the gaseous reaction products were continuously pumped (under a vacuum of the order of  $10^{-4}$  mm Hg) from the reaction space during the experiment. The carbon dioxide was collected in a trap cooled with liquid nitrogen, and its amount was periodically determined from the pressure after thawing and from the known volume. In order that an experiment could be carried out continuously, several traps connected in parallel were used.

Figure 1 shows the change in the rate of reduction of the nickel ferrite by graphite at  $950^\circ$  as a function of the amount of oxygen removed. In the beginning, up to 20% oxygen removal, some decrease in the rate was observed. After 45-50% of the oxygen had been removed from the sample, the reduction rate increased considerably, reaching a maximum at 80%.

Kinetics of such type indicate that crystallochemical conversions play a substantial role in the process of reduction.

The solid products from the reduction of nickel ferrite at different stages of reduction were investigated by x-ray techniques. The phase composition and the lattice parameter were determined.

It was found that the product of the reduction of nickel ferrite by graphite in the first stages of the reduction (up to 20%) is almost pure metallic nickel with a lattice parameter of  $3.517\text{--}3.520 \text{ \AA}$ . After 20% reduction, an increase in the lattice parameter of the metal phase was observed, which indicates an increase in the iron content of the nickel.

The dependence of the lattice parameter of the metallic phase on the oxygen content of the solid phase is shown in Figure 2. Up to 20% reduction, the concentration of iron in the nickel, calculated by the method of Bradley, Jay and Taylor [2], did not exceed 3 atom %, while at 35% reduction it was 20 atom %. On further reduction of the nickel ferrite, the lattice parameter of the metallic phase remained unchanged, and only after 50% reduction did it again begin to increase, attaining a value of  $3.581 \text{ \AA}$  at 70% reduction. This value of the lattice



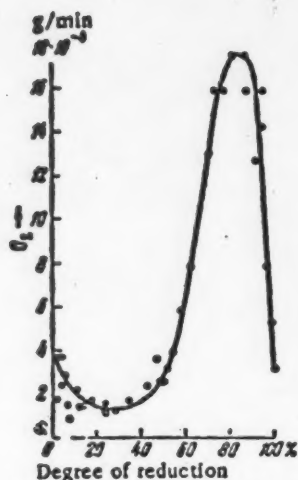


Fig. 1. Change in the rate of reduction of nickel ferrite by graphite at 950°.

parameter is close to the value for the parameter of the face-centered crystal lattice of the solid solution in the two-phase region of the structural diagram of the system Fe - Ni, and it corresponds to the limiting concentration of iron in nickel at room temperature.

The lattice parameter of the spinel phase of the original ferrite increased from 8.333 Å at the beginning of the reduction to 8.362 Å at 20% reduction, and then remained constant with further reduction of the ferrite (Figure 3).

A wüstite phase appeared in samples which were 35% reduced. At 50% reduction, a considerable amount of wüstite was observed along with the metallic and ferric phases.

Very small amounts of a metallic phase, a solid solution of nickel in iron with a body-centered lattice, was observed at 70% reduction.

The change in the lattice parameters of the spinel phase and the metallic reduction products indicates that the process of the reduction of nickel ferrite by

graphite at 1000° is accompanied by diffusion of metal ions in the crystal lattice.

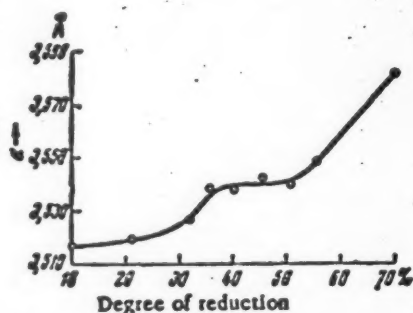


Fig. 2. Change in the lattice parameter of the metallic phase in the products of the reduction of nickel ferrite by graphite at 950°.

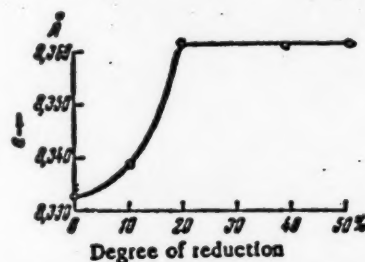


Fig. 3. Change in the lattice parameter of nickel ferrite during reduction by graphite at 950°.

As a result of the extraction of oxygen by the reducing agent, the surface layer of the ferrite is enriched in  $\text{Ni}^{2+}$  and  $\text{Fe}^{2+}$  ions. Some of these excess ions form the metallic phase; others diffuse into the depths of the crystal lattice. Both of these processes decrease the free energy of the surface layer, which had been increased by the excess of metallic ions. Those ions which are less strongly bonded by oxygen, i. e., nickel ions, predominantly migrate into the metallic phase. The iron ions, under the influence of the concentration gradient, diffuse inside the ferrite lattice. This process is accompanied by an increase in the lattice parameter of the ferrite, which approaches that of magnetite. The rate of reduction gradually decreases in this stage.

After 20% reduction of the ferrite, the lattice parameter of the spinel phase undergoes no further change, which indicates a cessation of the replacement of the nickel ions in the ferrite by iron ions. Since the ferrite is by now impoverished in nickel, on further reduction of the ferrite, iron ions become predominant in the reduction products, and these iron ions, dissolving in the nickel, increase the lattice parameter of the metallic phase.

The transition of magnetite to wüstite proceeds, as is well known [1], by diffusion of iron ions into the depth of the crystal lattice. Therefore, in the region of from 35-50% reduction, in which reduction of magnetite to wüstite takes place, no enrichment of the metallic phase by iron was observed, and the lattice parameter remained constant. Only after all of the magnetite was converted to wüstite, i. e., after 50% reduction, did the iron ions resulting from the reduction again diffuse into the metallic phase, a process which was accompanied by an increase of the lattice parameter. The kinetic picture of the reduction after 50% reduction corresponds to reduction of wüstite.

When the concentration of iron in nickel reached the maximum solubility of iron in the face-centered lattice of the solid solution, a phase with the body-centered lattice of  $\alpha$ -iron appeared in the metallic products of the reduction; this phase was formed at the expense of further reduction of the wüstite and also, possibly, at the expense of the decomposition of the supersaturated  $\gamma$ -solid solution of iron in nickel.

Thus, the mechanism of the reduction of nickel ferrite by graphite under vacuum is determined both by the diffusion of ions in the surface layer and by volume diffusion of ions into the depth of the crystal lattice. It is different from the case of reduction by gases, for example, by hydrogen at 400°, in which volume diffusion has no essential significance and in which lattice transformation is accomplished mainly through surface diffusion of ions.

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## ISOTOPE EXCHANGE OF MOLECULAR NITROGEN OVER IRON AMMONIA-SYNTHESIS CATALYST

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It has been established [1-3] that  $K_2O$  and  $Al_2O_3$  promoters for iron catalysts increase the specific activity (the activity per unit surface of catalyst) for the synthesis of ammonia at high pressures. Singly and doubly promoted catalysts have been shown to be considerably more active than unpromoted iron catalyst, and the promoting action of  $K_2O$  is greater than that of  $Al_2O_3$ .

With respect to the action of these promoters on the activity of the catalyst for ammonia synthesis at atmospheric pressure, the literature data are contradictory.

A brief communication by A. V. Krylova and S. Z. Roginskii [4] was devoted to clarification of the effect of these promoters on the rate of isotope exchange in molecular nitrogen; these authors came to the conclusion that unpromoted iron has greater specific activity than promoted catalysts. However, in work reported in reference [5], doubly promoted catalyst was found to be 10 times more active than unpromoted iron.

In this connection, the necessity arose for additional, broader investigation of isotope exchange in molecular nitrogen over iron catalysts promoted with different amounts of promoters — catalysts over which ammonia synthesis has been studied at high pressures [2, 3].

### EXPERIMENTAL

The experimental method has been described in detail [5]. A feature of the present investigation was that all samples, 30 g each, were reduced with hydrogen in a separate apparatus for 50-55 hours at  $500^\circ$ ; the space rate was  $6000 \text{ hours}^{-1}$  for 10 hours, and  $3000 \text{ hours}^{-1}$  for the remainder of the time.

At the conclusion of the reduction, the catalysts were passivated at room temperature with cylinder nitrogen using oxygen-free hydrogen as a diluent. The passivated samples were charged to the apparatus used for the study of isotope exchange, and were treated with hydrogen (activation) at  $500^\circ$  and a space rate of  $3000 \text{ hours}^{-1}$  for 10-15 hours.

The true order of the reaction, i. e., the dependence of exchange rate on total gas pressure, was determined over a pressure interval of 3-30 mm Hg, and the activation energy was determined in the temperature interval  $450-500^\circ$ .

The specific rate constant for the exchange (the catalyst activity) was calculated by means of an equation describing homomolecular isotope exchange [5, 6].

Table 1 presents the activation energy, the order of the reaction, and the specific catalytic activity,  $K(P, t)$ , at the corresponding pressure and temperature for the catalyst samples studied.

It should be pointed out that during the course of the tests, the activity of the catalyst promoted only with  $K_2O$  decreased substantially owing to partial volatilization of the promoter and to a decrease in the surface of this sample. Therefore, the initial and final activity of this catalyst are reported in the table.

TABLE 1

Kinetic Characterization of Isotope Exchange in Molecular Nitrogen Over Iron Catalysts

Sample No.	Promoter content, %		S <sub>sp.</sub> , sq m / g	E, kcal / mole	Order of reaction	Activity, cc/sq m / hour	
	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O				K (4,5mm500°)	K (3,3mm500°)
Armco	—	—	0,5	39*	0,9*	3,8·10 <sup>-3</sup> *	3,9·10 <sup>-3</sup>
16-55	Trace	2	1,2—0,6	35	0,75	4,1—0,3·10 <sup>-1</sup>	
4-55	3,8%	2,14	11	44	0,5	2,6·10 <sup>-3</sup>	
2-55	4,2	Trace	11,6	43	0,5	2·10 <sup>-3</sup>	
5-55	1,2	2,6	3,6	41,5	—	2,6·10 <sup>-3</sup>	

\*From reference [5].

## DISCUSSION OF RESULTS

From the data of Table 1, it is possible to form the general conclusion that promoted catalysts significantly exceed Armco Iron (unpromoted) with respect to specific activity. This is in agreement with the results obtained by us earlier [5].

Consequently, there is a quite definite parallel between the accelerating effect of promoters (K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>) on ammonia synthesis and the effect on isotope exchange. This fact is difficult to explain if it is assumed [7, 9] that the limiting stage in ammonia synthesis over iron catalysts is the hydrogenation of adsorbed nitrogen.

If it is assumed that isotope exchange and ammonia synthesis proceed through a common stage — adsorption of nitrogen — it is possible to compare quantitatively the rates of isotope exchange and ammonia synthesis taking into account filling of the catalyst surface with adsorbed nitrogen [5].

Calculation shows that the absolute reaction rates of ammonia synthesis and isotope exchange at the same coverage of adsorbed nitrogen are close in value over the singly promoted samples and Armco Iron\*.

In the case of the doubly promoted sample (3.85% Al<sub>2</sub>O<sub>3</sub> and 2.14% K<sub>2</sub>O), the rate of exchange was approximately half an order of magnitude less than the synthesis rate. A similar result has been obtained [5] for another catalyst (2% K<sub>2</sub>O and 4.5% Al<sub>2</sub>O<sub>3</sub>). However, a sample with different promoter contents (2.6% K<sub>2</sub>O and 1.2% Al<sub>2</sub>O<sub>3</sub>) was very active in exchange (Table 1).

The decreased activity in isotope exchange of the above-indicated doubly promoted sample could be due to insufficient mobility of chemisorbed nitrogen atoms on the surface of the catalyst. That ammonia synthesis can proceed over this catalyst by means of chemisorbed molecular nitrogen is also not excluded.

The kinetics of isotope exchange over these promoted catalysts are not in bad agreement with kinetics of ammonia synthesis. The activation energies of both processes, calculated at constant fugacity of adsorbed nitrogen, are in satisfactory agreement.

Thus, the experimental data on isotope exchange over iron ammonia-synthesis catalysts confirm the mechanism of Temkin and Pyzhev [10] for the synthesis of ammonia.

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# THE KINETIC ISOTOPE EFFECT IN IODINATION REACTIONS OF AROMATIC AMINES

F. M. Vainshtein and Academician AN UkrSSR E. A. Shilov

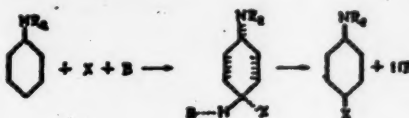
It was shown recently [1] that iodination reactions of aromatic dialkylaminosulfonic acids are described by the third-order kinetic equation

$$-\frac{d(I)}{dt} = k_1 [M]^2 [X] + k_2 [M] [X] [B], \quad (1)$$

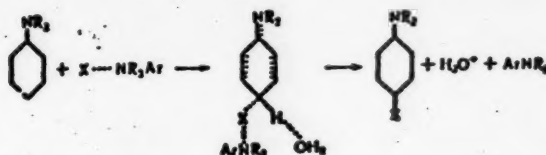
where M is the anion of the dialkylaminosulfonic acid, B is the basic component of the buffer solution, and X is an iodine cation or molecular iodine. It follows from Equation (1) that the base B or a second molecule of the amine takes part in the mechanism of iodination.

Two different explanations can be given.

A. The base serves as a proton acceptor according to:



B. The iodinating agent is a complex of the composition  $X \cdots NR_2Ar$  or, in buffer solutions,  $X \cdots B$ :



In this case, a molecule of water (as in the scheme) or another base can be the proton acceptor.

Schemes A and B are kinetically indistinguishable, but it is possible to make a choice between them by determining the isotope effect during replacement of hydrogen by iodine. In fact, if the reaction follows mechanism A, the isotope effect should be observed, since the splitting out of a proton is the stage which determines the over-all rate of the reaction (because the second molecule of amine or the base B enters into the kinetic equation). If B is the correct mechanism, the isotope effect does not necessarily occur, because the stage in which the proton is split out is not reflected in the kinetic equation. However, iodination by mechanism B can be accompanied by the isotope effect under conditions such that the rate of the removal of the proton is commensurate with the rate of formation of the intermediate quinoid complex.

With the aim of choosing between these alternative mechanisms, we studied the kinetics of the iodination of several aromatic amines and aminocarboxylic and aminosulfonic acids (see Table 1), and, in conjunction with this, the kinetic isotope effect was determined by comparing the iodination rate constants for the ordinary and deuterated amino compounds. It was established that the rate of iodination of these compounds, with the exception of certain particular cases and conditions which are discussed below, generally follow Equation (1). In this,

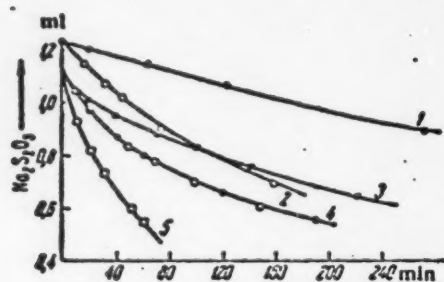


Fig. 1. Rate of iodination of amino compounds: 1) light aniline; 2) 2, 4, 6-trideuterioaniline; 3) light sodium m-aminobenzoate; 4) sodium salt of N, N-dimethylsulfanilic acid (open points represent the light salt; solid points represent the 2, 4, 6-trideuterio salt); 5) sodium salt of 2, 4, 6-trideuterio-m-aminobenzole acid

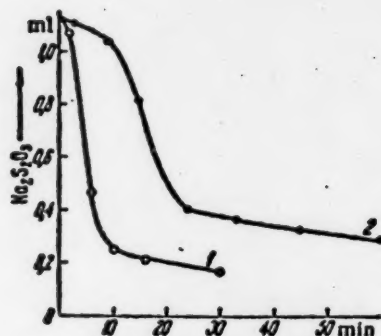


Fig. 2. Iodination of dimethylaniline. Initial concentrations (moles/liter): dimethylaniline, 0.0039;  $I_2$ , 0.0015; KI, 0.4; phosphate, 0.04; pH, 6.1; 30°. 1) light dimethylaniline; 2) 2, 4, 6-trideuteriodimethylaniline

TABLE 1

Compound	% replacement of H by D	$k_H/k_D$	Relative activity, $A_k$	Initial concentrations (moles/liter), pH, temperature
2,4,6-Trideuterio-N,N-dimethylmetanilate ion	90	1	1	M 0.0758; $I_2$ 0.003; KI 0.04; 25°
4-deuterio-N,N-dimethylmetanilate ion	61	1	1	M 0.0145; $I_2$ 0.0072; KI 0.073; phosphate 0.064; pH 6.9; 25°
2,6-dideuterio-N,N-dimethylsulfanilate ion	90	1	0.2	M 0.027; $I_2$ 0.005; KI 0.01; 25°
2,4,6-trideuterio-m-dimethylaminobenzoate ion	95	1.4	35	M 0.02; $I_2$ 0.005; KI 0.04; 30°
2,4,6-trideuteriometanilate	61	2*	0.02	M 0.133; $I_2$ 0.015; KI 0.036; 35°
2,4,6-trideuterio-m-aminobenzoate ion	90	4.8	0.22	M 0.045; $I_2$ 0.005; KI 0.05; 30°
Same	90	3.0	0.24	M 0.01; $I_2$ 0.005; KI 0.02; phosphate 0.1; pH 7.4; 30°
2,4,6-trideuterioaniline	86	3.5	5.4	M 0.025; $I_2$ 0.005; KI 0.15; 25°
Same	86	4.0	15	M 0.02; $I_2$ 0.004; KI 0.12; phosphate 0.025; NaCl 0.08; pH 8.0; 25°
2,4,6-trideuteriomethylaniline	95	3.2	110	M 0.01; $I_2$ 0.003; KI 0.3; acetate 0.05; pH 5.0; 25°
2,4,6-trideuteriodimethylaniline	89	3.0	120	M 0.01; $I_2$ 0.002; KI 0.15; lactate 0.5; pH 3.5; 30°

\* This value of the isotope effect is apparently lower than the true value, as in the preparation used the % replacement of H by deuterium was small.

X is the iodine cation (hydrated or complexed with the amine) for the primary amines and methylaniline. Iodination of the tertiary amino compounds proceeds by two routes — through  $I^+$  and through  $I_2$  (or their complexes with amines).

The basic results of the experiments are presented in Table 1 and Figure 1. The experimental conditions, the percentage replacement of hydrogen in the deuterio compounds, the isotope effect ( $k_H/k_D$ ), and the relative activity of the light amino compounds ( $A_k$ ) are shown in the table. The values of  $A_k$  are given with respect to the iodination rate of the N,N-dimethylmetanilate ion, which was taken as unity. The values of  $A_k$  must be con-

sidered as approximate; an accurate comparison was made difficult by the necessity of using very different iodination conditions for the different amino compounds.

As Curve 4 of Figure 1 and the data of Table 1 show, in certain cases the iodination reaction proceeds without any isotope effect ( $k_H/k_D = 1$ ). This applies to the three dimethylaminobenzenesulfonic acids. The 2, 4, 6-trideuterio-m-dimethylaminobenzoate ion iodates only a little slower than the light compound. Iodination proceeds with a significant isotope effect (from 3 to 4.8) for the remaining amino compounds. In this group are the various primary and secondary amines and the salts of aminosulfonic and aminocarboxylic acids containing a primary amino group.

That the isotope effect does not occur for certain amino compounds shows, as indicated above, that the base participates in the reaction as a component part of the iodinating complex, and not as a proton acceptor. The presence of an isotope effect with other amines can be explained by a difference in the reaction mechanism; however, it is necessary to take into consideration the very great similarity in the kinetic relations of the amines investigated. Therefore, we assume that in all cases iodination scheme B is correct, i. e., that the iodinating agents are complexes of an iodine cation or of iodine with the amino compound or with the base B.

In support of this conclusion, it is possible to cite other considerations [1]. In particular, calculation shows that under conditions close to those of our experiments, the concentration of  $I^+$  is  $10^{-14}$ – $10^{-15}$  M. Such an insignificant concentration of the active agent probably could not provide the observed iodination rate. On the other hand, the formation of complexes between amines and halogens is a general rule [3], and cases are known where the presence of amines in aqueous solution accelerates halogenation reactions [2].

We note that a kinetic isotope effect of 4 has also been found for the iodination of deuterated phenol [4], which is similar to the iodination of primary and secondary amines. Thus, iodination is among those few electrophilic hydrogen-replacement reactions in aromatic systems for which a kinetic isotope effect has been found. As is well known, nitration [5], bromination [6], and, for the most part, azo coupling [7] reactions proceed at the same rate for the light and heavy compounds. Sulfonation reactions [8] and cyclodehydrogenation of anils [9] have small isotope effects. The considerable isotope effect established for the case of azo coupling of p-chlorobenzenediazonium salts with 2-naphthol-6, 8-disulfonic acid in the presence of pyridine has found explanation in steric hindrance [7].

At the present time, it is not clear why the iodination of amines is connected with an isotope effect in some cases and not in others. As may be seen from the data of Table 1, there is no general relationship between reaction rate and isotope effect. Thus, for example, an isotope effect is observed both for the very slightly active metanilic acid and for the very active methylaniline and dimethylaniline. Between these extremes, the fairly active dimethylaminobenzenesulfonic acid salts are iodinated at the same rate in the light and heavy forms. It is possible that the relationship between iodination rate and isotope effect must be considered separately for primary and secondary amines as opposed to tertiary amines.

#### EXPERIMENTAL\*

Preparations of m- and p-dimethylaminobenzenesulfonic acids were obtained by sulfonation of dimethylaniline [10]. m-Dimethylaminobenzoic acid was prepared from m-aminobenzoic acid by methylation with methyl iodide in alkaline medium [11]. The monomethyl derivative was separated by extraction of the dimethylaminobenzoic acid from the aqueous solution at a pH of about 4 with ether; the compound was in the form of long, fine needles with a m. p. of  $154^\circ$ . As for the other amino compounds, commercial preparations were used after the requisite purification.

The 2, 4, 6-trideuterio derivatives of aniline, methylaniline, and dimethylaniline, as well as the 2, 4, 6-trideuterio-m-amino- and m-dimethylaminobenzoic acids were prepared by exchange between the light compounds and 99%  $D_2O$  in acid medium by heating to  $100^\circ$  over a period of 60–100 hours. 2, 4, 6-trideuterio-m- and p-dimethylaminobenzenesulfonic acids were prepared by sulfonation of 2, 4, 6-trideuteriodimethylaniline with 30% deuteriooleum which was prepared from  $SO_3$  and  $D_2O$ . 4-Deuterio-N,N-dimethylmetanilic acid

\*With the assistance of O. M. Grishin.



was prepared by sulfonation of 4-deuteriodimethylaniline, which was obtained from p-bromodimethylaniline through p-dimethylaminophenyllithium [12]. The deuterium content of these preparations was determined from the combustion water by the flotation, mass spectroscopic, or falling drop method.

The iodination rate was measured at different concentrations of amino compound, iodine, and potassium iodide without added material and in the presence of phosphate, acetate, or lactate as a buffer. The drop in the iodine titer was determined by microtitration of samples with thiosulfate.

For the most part, the results of the kinetic experiments were readily reproducible and permitted precise establishment of the dependence of reaction rate on the concentrations of the components of the mixtures. These data will be presented in detail in another place. In this article, we merely point out that during iodination of methylaniline and dimethylaniline, the reaction, under certain specific conditions, is autocatalytic, as may be seen from Figure 2. The reaction proceeds normally according to Equation (1) if it is carried out at low concentrations of free amine and iodine. The values of  $k_H/k_D$  presented for these two amines in Table 1 were obtained under conditions such that autocatalysis did not occur, in particular, at low pH. Figure 2 shows, however, that the autocatalytic reaction also proceeds with an isotope effect of 3-4. The nature of the autocatalytic reaction is not altogether clear.

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## NITROBENZALDEHYDES IN THE REFORMATSKY REACTION

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(Presented by Academician B. A. Kazanskii, May 23, 1958)

Attempts to introduce carbonyl compounds containing a nitro group into the Reformatsky reaction have thus far been unsuccessful [1]. The use of these compounds in Grignard reactions has also given unsatisfactory results [2]. However, the reasons for these failures are not the same in the two cases.

In Grignard reactions, the difficulty is the reduction of the nitro group by the Grignard reagent. This difficulty was surmounted by carrying out the reaction at low temperature [2]. Consequently, the presence of a nitro group does not prevent reactions of organometallic compounds with a carbonyl group.

In Reformatsky reactions with carbonyl compounds containing a nitro group, practically all of the zinc remains unchanged. Since here the composite organozinc compound must be formed in the presence of a carbonyl compound, it may be assumed that a nitro group in the carbonyl compound hinders the interaction of the zinc with the halo ester.

This was confirmed by the fact that the readily occurring reaction of acetophenone with bromoacetic ester is completely arrested by the addition of 0.05 mole of nitrobenzene, even if the reaction is carried out in tetrahydrofuran in the presence of mercuric chloride, which, as is well known, facilitates the course of the reaction [3].

It is evident that a Reformatsky reaction involving a carbonyl compound containing a nitro group should be carried out in two stages, first, the preparation of the "Reformatsky reagent" from zinc and the halo ester and, second, the reaction of the reagent with the carbonyl compound.

We used for this purpose the method of Siegel and Keckels [4] which was developed by them for carrying out Reformatsky reactions with quinol reactions in which it is necessary to exclude reduction of the quinols by zinc. Using this method, we were able to prepare the corresponding esters of  $\beta$ -hydroxy- $\beta$ -nitrophenylpropionic acid from o-, m-, and p-nitrobenzaldehydes and bromoacetic ester. That these reactions were successfully carried out confirms the above assumption that the nitro group hinders the formation of the composite organozinc compounds.

### EXPERIMENTAL

8 g of zinc turnings were washed with a mixture of acetone and 2% hydrochloric acid, then with acetone and dried with a heat lamp; to these turnings in 100 ml of dry ether were added 5 drops of an ethereal solution of  $\text{CH}_3\text{MgI}$  and then 10 g (0.06 mole) of bromoacetic ester, and the mixture was refluxed for 2-2.5 hours with stirring. The resulting solution of "Reformatsky reagent" was decanted from the unreacted zinc (~5.5 g) into 4.5 g (0.03 mole) of o-, m-, or p-nitrobenzaldehyde and the reaction mixture was refluxed for 1 hour, cooled, and stirred for 30 minutes with 50 ml of 10% acetic acid; the water layer was separated, extracted with ether, and the ether extract was added to the ether layer. The ether solution was agitated for 30 minutes with 5 ml of a solution of sodium bisulfite, washed with water, a 10% solution of soda, and again with water and dried with anhydrous magnesium sulfate; the ether was distilled, and the residue was distilled under vacuum.

Properties of the products are presented in Table 1. About 1 g of unreacted aldehyde was separated by soda from the bisulfite extract.

TABLE 1

Original nitrobenzaldehyde	Product obtained	Yield		B. p.	M. p.	
		g	%		Our data	Lit. data
Ortho-	Ethyl $\beta$ -hydroxy- $\beta$ -(o-nitrophenyl) propionate	3.0	41.9	170-175°/5 mm	Liquid*	Amide m. p. 197° [5]
Meta-	Ethyl $\beta$ -hydroxy- $\beta$ -(m-nitrophenyl) propionate	3.5	48.9	179-182°/2.5 mm	58° (from alcohol)	55° [6]
Para-	Ethyl $\beta$ -hydroxy- $\beta$ -(p-nitrophenyl) propionate	3.6	50.3	184-186°/3 mm	46.5-47° (from ether)	45-46° [6]

\* Of aldehyde charged

\*\* 0.5 g of ethyl  $\beta$ -hydroxy- $\beta$ -(o-nitrophenyl) propionate, 1 ml of 25% aqueous ammonia, and 0.5 ml of methanol were allowed to stand for 48 hours; filtration gave 0.35 g of the amide of  $\beta$ -hydroxy- $\beta$ -(o-nitrophenyl) propionic acid. m. p. 197° (from alcohol).

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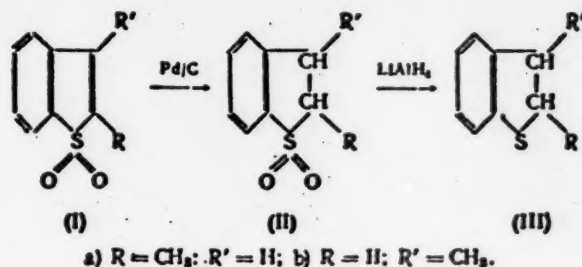
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# SYNTHESIS OF 2-METHYL- AND 3-METHYL-1-THIAINDANS AND 2-ETHYLTHIAINDENE

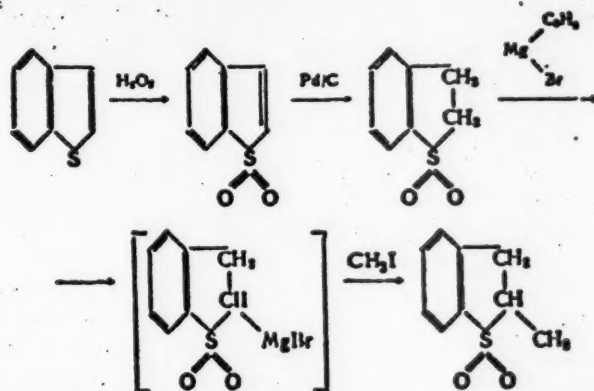
E. N. Karaulova, D. Sh. Mellanova and G. D. Gal'pern

(Presented by Academician A. V. Topchlev, June 14, 1958)

In connection with the study of sulfur compounds found in petroleum fractions, the so-called semiaromatic sulfur compounds, particularly the alkyl derivatives of 1-thiaindan (2, 3-dihydrothianaphthene) with substituents in the five-membered ring, are of interest as model compounds. In seeking a method for the synthesis of such compounds, we found that the presently unknown 2- and 3-methyl-1-thiaindans (III) can be smoothly prepared by stepwise reduction of the sulfones (I) of the corresponding 2- and 3-methylthiaindenes:



A satisfactory method of synthesis of 2-alkylthiaindenes is metalation of thiaindene (thianaphthene) with *n*-butyllithium and subsequent alkylation with dialkyl sulfates. By the action of dimethyl and diethyl sulfate on 2-thiaindenyllithium, we obtained, respectively, 2-methylthiaindene and the previously undescribed 2-ethylthiaindene. The 2-methylthiaindene was oxidized with hydrogen peroxide to 2-methylthiaindenesulfone (Ia). The structure of the 2-methyl-1-thiaindan (IIIa) was proved by alternate synthesis according to the scheme:



\* We have previously shown [1] that on hydrolysis, allyl phenyl sulfide forms not *o*-allylthiophenol with admixed 2-methyl-2, 3-dihydrothianaphthene, but, contrary to the data of Hurd and Greengard [2], propenyl phenyl sulfide and condensation products of the latter.



3-Methylthialindenesulfone (Ib) was synthesized by the method of Werner [3]: phenyl acetyl sulfide, prepared from chloroacetone and sodium thiophenolate, was cyclized through the action of  $P_2O_5$  to 3-methylthialindene and the latter was oxidized with  $H_2O_2$  to 3-methylthialindenesulfone. The structure of the 3-methyl-1-thialindan (IIb) was proved by hydrosulfurization over skeletal nickel; the yield of cumene was 84% of theoretical.

0.18 mole of thialindane was metalated with  $n-C_4H_9Li$  by the method of reference [4]. To an ether solution of 2-methylthialindenyllithium was added a solution of 0.18 mole of  $(CH_3)_2SO_4$  in 100 ml of ether; the solution was stirred for 1 hour, and then refluxed 0.5 hour. The ether was distilled, and the residue was added to a solution of  $C_2H_5ONa$  (from 0.1 mole of Na and 120 ml of alcohol) and refluxed for 0.5 hour. The mixture was treated with water, and extracted with ether. Distillation of the extract under vacuum gave 2-methylthialindene in 91% yield; b. p. 92-93°/5 mm, m. p. 51-52° (reference [4] gives 51.5-52.5° for the m. p.). 0.14 mole of 2-methylthialindene in glacial  $CH_3COOH$  was oxidized with a 200% excess of 27.3%  $H_2O_2$  for 1 hour at 100°. 2-Methylthialindenesulfone was obtained in 75% yield; m. p. 109-110° (from alcohol).

Found %: C 59.89; H 4.44; S 17.47

$C_9H_8SO_2$ . Calculated %: C 60.00; H 4.44; S 17.77

To an ether solution of 2-thialindenyllithium, obtained from 0.05 mole of thialindene, was added 0.075 mole of  $(C_2H_5)_2SO_4$  in 50 ml of ether. The mixture was refluxed 10 hours, and then treated in a manner similar to that described above and 81% yield of 2-ethylthialindene was obtained; b. p. 95-96°/1.5 mm,  $n_D^{20}$  1.6063.

Found %: C 73.93; H 6.31; S 19.72

$C_{10}H_{10}S$ . Calculated %: C 74.07; H 6.17; S 19.75

The 2-ethylthialindene was oxidized similarly to the 2-methylthialindene; the yield was 77%, m. p. 86.5-87.5° (from alcohol).

Found %: C 61.86; H 5.15; S 16.31

$C_{10}H_{10}SO_2$ . Calculated %: C 61.86; H 5.16; S 16.49

A solution of 0.55 mole of 2-methylthialindene in 700 ml of alcohol was hydrogenated over a 10 hour period in the presence of 3 g of 5% Pd/C at an initial  $H_2$  pressure of 50 atm. Most of the alcohol was distilled and the residue was diluted with water to precipitate the 2-methyl-1-thialindansulfone; the yield was 95%, m. p. 115-115.5° (from alcohol).

Found %: C 59.38; H 5.53; S 17.67; M 182

$C_9H_{10}SO_2$ . Calculated %: C 59.34; H 5.49; S 17.58; M 182

0.15 mole of 2-methyl-1-thialindansulfone in benzene was added to an ether solution of 0.23 mole of  $LiAlH_4$  (in a manner such that the mixture boiled weakly), and the mixture was stirred for 2 hours. The mixture was then diluted with water and steam-distilled; the distillate was extracted with ether. The extract was dried with  $MgSO_4$  and distilled; an 81% yield of 2-methyl-1-thialindan was obtained; b. p. 118-120°/21 mm,  $n_D^{20}$  1.5905. The 2-methyl-1-thialindan was treated by heating with an alcoholic solution of mercuric chloride, and the resulting complex was separated; the yield was 80%, m. p. 115-116°. The complex was decomposed with 15% hydrochloric acid and the mixture was steam-distilled; a 45% yield of 2-methyl-1-thialindan was obtained, b. p. 123/24.5 mm,  $n_D^{20}$  1.5922,  $d_4^{20}$  1.0859.

Found %: C 72.04; H 6.70; S 21.08; M 149.8

$C_9H_{10}S$ . Calculated %: C 72.00; H 6.66; S 21.33; M 150

$MR_D$  found 46.76; calculated 45.94.  $EMRD$  calculated 0.82.

Thialindene was oxidized with  $H_2O_2$ ; the yield of thialindenesulfone was 75%, m. p. 141-142.5° (from alcohol); according to reference [5], m. p. 142-143°. 0.42 mole of thialindenesulfone was hydrogenated over a period of 4.5 hours in the presence of 3.5 g of Pd/C at an initial  $H_2$  pressure of 20 atm. A 97% yield of 1-thialindansulfone was obtained; m. p. 90-91° (from alcohol); according to reference [6], m. p. 91-92°.

To a solution of 2-thialindansulfonylmagnesium bromide in benzene, prepared by the method of reference [6] from 0.03 mole of 1-thialindansulfone, was added 0.045 mole of  $CH_3I$ . The mixture was refluxed for 4 hours, and was then treated with water and extracted with benzene. The extract was dried with  $MgSO_4$ , the solvent dis-



tilled, and the residue twice recrystallized from alcohol to give a yield of 2-methyl-1-thialindansulfone of 40% of theoretical; m. p. 114-115°. A mixed sample with the sulfone obtained by hydrogenation of 2-methyl-thialindenesulfone showed no depression of the melting point.

0.08 mole of 3-methylthialindenesulfone in 750 ml of alcohol was hydrogenated over a period of 10 hours in the presence of 8 g of ~7% Pd/C at an initial  $H_2$  pressure of 35 atm; the yield (unpurified) was 97%, m. p. 57-58° (from alcohol-water, 1:3).

Found %: C 59.50; H 5.58; S 17.28

$C_9H_{10}SO_2$ . Calculated %: C 59.34; H 5.59; S 17.58

0.22 mole of 3-methyl-1-thialindansulfone in ether was added to an ether solution of 0.28 mole of  $LiAlH_4$  (while lightly boiling the ether); the mixture was then stirred not more than 10 minutes and was treated as in the case of 2-methyl-1-thialindansulfone; the yield of 3-methyl-1-thialindan was 70%; b. p. 94.5°/4.5 mm,  $n_D^{20}$  1.5953. An 87% yield of the complex with  $HgCl_2$  was obtained; m. p. 116-116.5° (from alcohol).

Found %: C 15.52; H 1.48; Hg 57.54

$C_9H_{10}S \cdot 2HgCl_2$ . Calculated %: C 15.58; H 1.44; Hg 57.86

3-Methyl-1-thialindan was recovered from the complex in 67% yield; b. p. 96.5-97°/6 mm,  $n_D^{20}$  1.5969,  $d_4^{20}$  1.0980.

Found %: C 72.09; H 6.76; S 21.11; M 148.7

$C_9H_{10}S$ . Calculated %: C 72.00; H 6.66; S 21.33; M 150

$MR_D$  found 46.54; calculated 45.94;  $E_{MR_D}$  calculated 0.60.

The 3-methyl-1-thialindan was oxidized with  $H_2O_2$  to 3-methyl-1-thialindansulfone; the yield was 70%.

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## CATALYTIC SYNTHESIS OF 4-METHYL-2-PHENYL-5,6-BENZOQUINOLINE AND 2,4-DIPHENYL-5,6-BENZOQUINOLINE AND THEIR DERIVATIVES

N. S. Kozlov and I. A. Shur

(Presented by Academician A. A. Balandin June 14, 1958)

As is well known, the synthesis of 5,6-benzoquinoline and its derivatives is accomplished by ordinary methods of synthesis of quinoline compounds [1]. Among the known methods, the most satisfactory method for the preparation of 2-methyl-5,6-benzoquinoline and its derivatives is the method of Döbner [2, 3], the basis of which is the condensation of 2-naphthylamine and various aromatic aldehydes with pyruvic acid. The 2-phenyl-5,6-benzoquinoline-4-carboxylic acid and its derivatives formed by this reaction readily undergo decarboxylation on heating, being converted thereby to 2-phenyl-5,6-benzoquinoline and its derivatives.

But the method of Döbner cannot be considered ideal, since the synthesis of the quinoline base is carried out in two stages, which complicates the reaction and lowers the yield of the end products.

A new method has recently been developed for the synthesis of 2-phenyl-5,6-benzoquinoline and its derivatives by catalytic condensation of 2-naphthylamine and various aromatic aldehydes with acetylene [4, 5].

It should be noted, however, that the synthesis of 4-methyl-2-phenyl-5,6-benzoquinoline and 2,4-diphenyl-5,6-benzoquinoline and their derivatives has not yet been developed sufficiently [1]. We are aware only of the work of John and Hoziczka, who obtained a small yield of 4-methyl-2-phenyl-5,6-benzoquinoline by heating benzalacetone and 2-naphthylamine in a sealed tube, and the work of Dziewonski [7], who accomplished the synthesis of 2,4-diphenyl-5,6-benzoquinoline by the condensation of 1-benzoyl-2-aminonaphthalene with acetophenone.

It is well known that the 5,6-benzoquinoline nucleus is present in the composition of the physiologically active alkaloids of ergot and other plants. Therefore, it may be assumed that 5,6-benzoquinoline derivatives should also possess bactericidal properties. Hence, the development of new methods of synthesis of 4-methyl-2-phenyl-5,6-benzoquinoline and 2,4-diphenyl-5,6-benzoquinoline and their derivatives must be of scientific and practical interest.

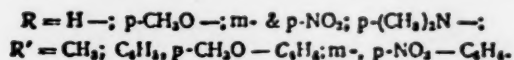
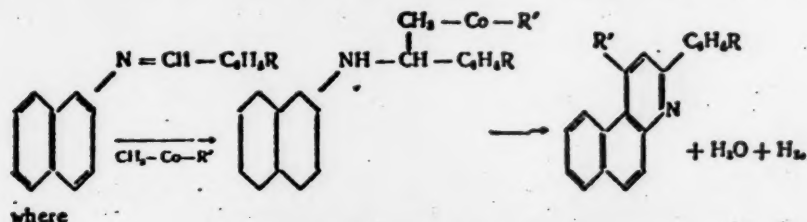
In setting up the present work, we were guided by the theoretical considerations which were previously published by one of us [8]. We felt that Schiff bases, under appropriate conditions, would condense with acetone and acetophenone forming beta-arylamino ketones which, by cyclization, could be converted to diphenyl derivatives of quinoline. This reaction should proceed especially easily with the products of the interaction of acetophenone with Schiff bases obtained from 2-naphthylamine and aromatic aldehydes in view of the exceptional tendency of compounds of similar nature toward cyclization at the alpha position of the naphthalene ring [1].

Our experiments confirmed the correctness of the above. Indeed, under appropriate conditions, Schiff bases from 2-naphthylamine and aromatic aldehydes — benzaldehyde, anisaldehyde, m- and p-nitrobenzaldehydes, and p-dimethylaminobenzaldehyde — react with acetone and acetophenone forming 2,4-diphenyl-5,6-benzoquinoline and 4-methyl-2-phenyl-5,6-benzoquinoline and 4-methyl-2-phenyl-5,6-benzoquinoline and their p-methoxy, p-dimethylamino, and m- and p-nitro derivatives. The majority of these compounds were prepared for the first time. The catalyst used in this reaction was 2-naphthylamine hydrochloride.

TABLE 1

Substance and its empirical formula	Melting point, °C			Product Yield, %	N, %		Pt in platinates, %		
	Experimental	Literature	Hydrochloride		Picrate	Calc.	Found	Calc.	Found
4-Methyl-2-phenyl-5,6-benzoquinoline, $C_{17}H_{15}N$	152—155	152	205	224	41.2	5.21	20.16	20.27	
4-Methyl-2-(4-methoxyphenyl)-5,6-benzoquinoline, $C_{18}H_{17}NO$	124	—	240	225 with decompa.	20.0	4.53	19.56	19.58	
4-Methyl-2-piperonyl-5,6-benzoquinoline, $C_{18}H_{15}NO_2$	161—162	—	275	203 with decompa.	23.5	4.47	18.84	19.04	
4-Methyl-2-(3-nitrophenyl)-5,6-benzoquinoline, $C_{17}H_{14}N_2O_2$	178	—	231—233	220	47.4	8.92	18.80	18.53	
4-Methyl-2-(4-nitrophenyl)-5,6-benzoquinoline, $C_{17}H_{14}N_2O_2$	192	—	237—238	228	34.4	8.92	18.80	18.03	
2,4-Diphenyl-5,6-benzoquinoline, $C_{19}H_{17}N$	144—145	144	—	231	40.0	4.23	18.20	18.50	
2-(4-Methoxyphenyl)-4-phenyl-5,6-benzoquinoline, $C_{20}H_{19}NO$	154—155	—	210	235 with decompa.	32.5	3.88	17.24	17.50	
2-(3-Nitrophenyl)-4-phenyl-5,6-benzoquinoline, $C_{19}H_{16}N_2O_2$	231	—	226	204	50.0	7.45	16.79	16.88	
2-(4-Nitrophenyl)-4-phenyl-5,6-benzoquinoline, $C_{19}H_{16}N_2O_2$	254	—	252	218—220	40.5	7.45	16.79	16.80	
2-(4-Dimethylaminophenyl)-4-phenyl-5,6-benzoquinoline, $C_{21}H_{22}N_2$	180	—	decomposed	decomposed	42.0	7.43	—	—	
						7.43		7.53	

The mechanism of these reactions can be represented by the following equations:



The reaction mechanism indicated above was confirmed by specially conducted experiments. For this purpose we developed a variant of the synthesis of beta-2-naphthylamino-beta-phenylpropophenone, which was converted by cyclization to 1,3-diphenyl-5,6-benzoquinoline.

#### DESCRIPTION OF THE METHOD

The synthesis of 4-methyl-2-phenyl-5,6-benzoquinoline and its derivatives was carried out by the following method. A reaction mixture consisting of 0.05 mole of the Schiff base, 0.05 mole of acetone, 10-20 ml of alcohol, and 1.0 g of 2-naphthylamine hydrochloride was heated on a water bath for 15-30 minutes. After the reaction mixture had been cooled, the precipitate was filtered, treated with aqueous ammonia, and crystallized from alcohol and toluene.

For the preparation of 2,4-diphenyl-5,6-benzoquinoline and its derivatives, a reaction mixture consisting of 0.05 mole of Schiff base, 0.05 mole of acetophenone and 1.0 g of 2-naphthylamine hydrochloride, was heated, in the absence of a solvent, at 160-180° for 15 minutes. Further treatment was as in the preceding case. The results obtained and the constants of the compounds synthesized are presented in Table 1.

Thus, in the present work, we were able to develop a new and extremely practicable and convenient method for the synthesis of 4-methyl-2-phenyl-5,6-benzoquinoline and 2,4-diphenyl-5,6-benzoquinoline and their derivatives and to synthesize ten compounds of this series, of which eight were previously undescribed. It is quite clear that the introduction into this reaction of other Schiff bases and the replacement of acetone and acetophenone by other ketones opens up new routes for the synthesis of varied and numerous derivatives of 5,6-benzoquinoline.

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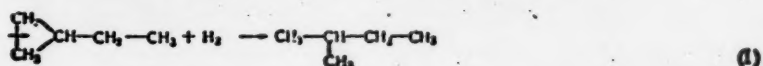


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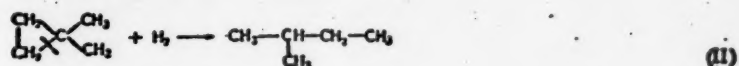
# THE EFFECT OF THE CATALYST SUPPORT ON THE COURSE OF THE CATALYTIC HYDROGENATION OF HYDROCARBONS OF THE CYCLOPROPANE SERIES

M. Iu. Lukina, S. V. Zotova and Academician B. A. Kazanskii

We have previously had occasion [1] to point out that the literature on the catalytic hydrogenation of cyclopropane hydrocarbons contains much contradictory data relating to the course of the rupture of the three-membered ring. The majority of authors consider that in this reaction, bond rupture and the addition of hydrogen across the bond occurs between the two most hydrogenated carbon atoms [1-6], for example:



However several cases of ring cleavage at other locations have also been described [7, 8]. In particular, Slobodin and co-workers [9] consider that during the hydrogenation of gem-dimethylcyclopropane in the presence of nickel deposited on kieselguhr, the reaction proceeds according to:



These authors came to the conclusion that in this case hydrogenolysis of the cyclopropane ring proceeds through an intermediate stage in which the alkylcyclopropane isomerizes to an olefin, which is then hydrogenated; the presence of olefin in the products of incomplete hydrogenation was shown by means of Raman spectra.

As to the causes of the different direction of cleavage of the three-membered ring, the authors expressed no opinions, and, apparently, tended to ascribe it to the structural features of the particular hydrocarbon.

There is, however, one important factor which can affect the direction of cleavage of the three-membered ring during hydrogenation, namely, the carrier of the hydrogenating metal, since the catalysts used are ordinarily supported catalysts. As we have previously shown, silica gel [10] and activated carbon [11] catalyze the isomerization of cyclopropane hydrocarbons to olefins, though under different conditions: silica gel catalyzes the reaction even at a temperature close to 0°, while activated carbon is active only at a temperature of about 200°. The isomerization proceeds by rupture of the C - C bond at the least hydrogenated carbon atom in the ring:



It is natural to assume that if the hydrogenating metal is deposited on a carrier which, like silica gel and activated carbon, is capable of causing isomerization of cyclopropane hydrocarbons to olefins, then in the presence of such catalysts and under suitable conditions, the direction of ring cleavage will be different than when an inert carrier is used. Indeed, in the first case, the olefin hydrogenated will be that which is formed by isomerization of the alkylcyclopropane (Equation III), while in the latter case, the cyclopropane hydrocarbon itself will be hydrogenated (Equation I). The relative isomerizing activity of such supported catalysts will determine the course of the cleavage of the three-membered ring.

In the present paper, we describe experiments on the isomerization of cyclopropane hydrocarbons to olefins

TABLE 1

Fraction No.	B. p., °C (760 mm)	Amount, g	$n_D^{20}$	$d_4^{20}$	Aniline point, °C
1	34.0-35.0	2.1	1.3610	0.6375	59.8
2	35.0-36.1	2.8	1.3620	0.6412	56.4
loss		0.2			

TABLE 2

Expt. No.	Run Temp. °C	Catalyzate properties		
		$n_D^{20}$	Bromine number	Content of unsaturated, %
1	120	1.3862	—	0
2	170	1.3889	38.4	20.1
3	220	1.3915	85.6	45.0

TABLE 3

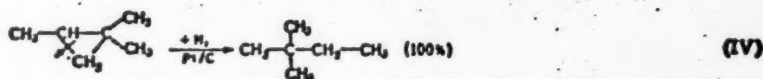
Fraction No.	B. p., °C (760 mm)	Amount, g	$n_D^{20}$	$d_4^{20}$
1	49.4-49.7	1.3	1.3689	0.6493
2	49.7-56.1	2.6	1.3705	0.6543
3	56.1-57.6	1.7	1.3742	0.6604
4	57.6	3.7	1.3746	0.6617
5	57.6-57.8	4.0	1.3748	0.6613
6	57.8-58.4	1.3	1.3742	0.6609
7	58.4-67.5	0.3	—	
loss		0.2		

TABLE 4

Hydrocarbon	B. p., °C (760 mm)	$n_D^{20}$	$d_4^{20}$
n-Pentane [15]	36.07	1.35745	0.62619
2-Methylbutane [15]	27.85	1.35669	0.61963
2,2-Dimethylbutane [15]	49.741	1.36876	0.64916
2-Methylpentane [15]	60.271	1.37145	0.65315
2,3-Dimethylbutane [15]	57.988	1.37495	0.66164

In the presence of such substances as aluminosilicate, kieselguhr, and pumice, which are frequently used as carriers for the preparation of hydrogenation catalysts. It was found that in the presence of aluminosilicate, ethylcyclopropane is almost completely isomerized to a mixture of olefins of normal structure even at 50°; over kieselguhr, isomerization proceeds to the extent of 75% at 120°, while over pumice, isomerization does not occur at all at 120° and proceeds to the extent of 20% at 170° and 45% at 220°.

If hydrogenation of cyclopropane hydrocarbons is carried out in the presence of platinumized carbon and platinumized kieselguhr at 150° i. e., at a temperature at which activated carbon does not isomerize hydrocarbons with a three-membered ring to olefins and kieselguhr promotes fairly extensive isomerization, then in the case of platinumized carbon, ring cleavage occurs only at the C—C bond between the most hydrogenated hydrocarbon atoms:



In the presence of platinumized kieselguhr, chiefly the other bonds of the three-membered ring are cleaved, and 2,2-dimethylbutane is formed in the amount of only 15%.

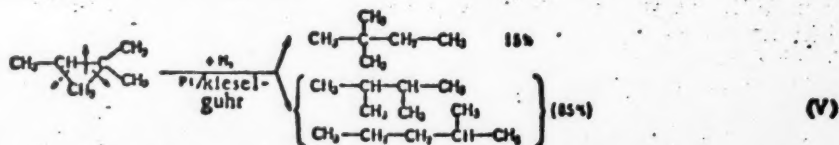


TABLE 5

Frac. tion No.	B. p., °C (760 mm)	Amount, g	$n_D^{25}$	$d_4^{25}$
1	30.9-35.1	1.9	1.3562	0.6235
2	35.1-35.9	3.2	1.3574	0.6256
3	35.9	1.4	1.3575	0.6261
4	35.9-36.1	3.9	1.3575	0.6262
5	36.1-36.9	0.4	1.3580	—

on pumice and by Benson and Kwan [14] in the presence of nickel on aluminosilicate. It should be pointed out that these and other authors consider that the mechanism of cyclopropane hydrogenation consists of collisions of molecules of gaseous cyclopropane with hydrogen atoms adsorbed on the catalyst, which leads to the formation of cyclopropyl or propyl radicals. However, some such reaction apparently took place in the experiments of Bond, while in Benson's experiments a different reaction occurred, since there hydrogenation was preceded by isomerization of the cyclopropane to propylene due to the aluminosilicate which formed part of the catalyst. Such a reaction occurred in the work of Slobodin and co-workers [9], cited above, where nickel on kieselguhr was used as the catalyst.

#### EXPERIMENTAL

**Isomerization of Ethylcyclopropane in the Presence of Aluminosilicate.** Ethylcyclopropane, with a b. p. of 35.5° (760 mm),  $n_D^{25}$  1.3786;  $d_4^{25}$  0.6841, and an aniline point of +17.9°, was passed at 50° and a space rate of 0.2 hours<sup>-1</sup> through a tube containing 10 ml of aluminosilicate catalyst. The resulting catalyze instantly decolorized bromine water, and, according to its bromine number, contained 88.4% unsaturateds.

**Isomerization of Ethylcyclopropane in the Presence of Kieselguhr.** "Kisatibi" grade kieselguhr was finely ground, wetted with water, formed into pellets (3 x 3 mm), and dried at 100°.

Ethylcyclopropane was passed at 75° and a space rate of 0.2 hours<sup>-1</sup> through a tube containing 10 ml of kieselguhr. The catalyze decolorized bromine water with difficulty. The catalyze obtained at 120° instantly decolorized bromine water, and had  $n_D^{25}$  1.3798 and  $d_4^{25}$  0.6659. The product of its hydrogenation over platinum black had a b. p. of 34.0-36.0°,  $n_D^{25}$  1.3624 and  $d_4^{25}$  0.6398. The following fractions were collected during distillation in a column of 40 theoretical plates (Table 1).

It is apparent from the properties of the fractions that the catalyze consisted of n-pentane and ethylcyclopropane. Calculation of the fractional composition from the specific volumes and aniline points showed that the catalyze contained 74.2% n-pentane and 25.8% ethylcyclopropane (the properties of n-pentane are given in Table 4).

**Isomerization of 1,1,2-Trimethylcyclopropane in the Presence of Pumice.** Pieces of pumice, 6 x 3 mm, were carefully purified by boiling with HCl and washing with water until reaction with CNS<sup>+</sup> was negative. After being dried at 120°, 10 ml of pumice was placed in the catalyst tube and heated to 300° in an atmosphere of nitrogen. 1,1,2-trimethylcyclopropane (b. p. 52.6° (760 mm),  $n_D^{25}$  1.3862,  $d_4^{25}$  0.6948) was passed through the pumice at temperatures of 120-220° and a space rate of 0.2 hours<sup>-1</sup>. The experimental results are presented in Table 2.

In these experiments, 1,1,2-trimethylcyclopropane was not isomerized at 120°, and at 170° and 220° it was isomerized to the extent of 20% and 45%, respectively.

**Hydrogenation of 1,1,2-Trimethylcyclopropane in the Presence of Platinized Kieselguhr.** 1,1,2-trimethylcyclopropane in a stream of hydrogen was passed at 150° and a space rate of 0.2 hours<sup>-1</sup> through a tube containing 10 ml of platinized "Kisatibi" kieselguhr (20% Pt).

The saturated catalyze ( $n_D^{25}$  1.3740,  $d_4^{25}$  0.6583) was distilled in a column of 40 theoretical plates (Table 3).

The constants of the hydrocarbons which could be formed from ethylcyclopropane and 1,1,2-trimethylcyclopropane are presented in Table 4.

Thus, there is no doubt of the effect of an active carrier (active in the sense of isomerization) on the course of the hydrogenolysis of a three-membered ring. This can explain the different results obtained when kieselguhr or aluminosilicate was used as the carrier, as opposed to the case when pumice or activated carbon was used, the hydrogenating metal being the same in both cases.

Apparently this can also explain the differences in the kinetics of cyclopropane hydrogenation observed by Bond and co-authors [12,13] in the presence of nickel



On the basis of a comparison of the data of Tables 3 and 4, it can be concluded that Fraction 1 consisted of 2,2-dimethylbutane, which was also present in Fraction 2. Fractions 3, 4, and 5 consisted mainly of 2,3-dimethylbutane. Fractions 6 and 7 also contained 2-methylpentane. Thus, the catalyzate consisted of approximately 15% of the product of direct hydrogenolysis (2,2-dimethylbutane) and 55% of the product of isomerization to olefins and subsequent hydrogenation (2,3-dimethylbutane and 2-methylpentane).

Hydrogenation of Ethylcyclopropane in the Presence of Platinized Kieselguhr was carried out in the same manner as the hydrogenation of 1,1,2-trimethylcyclopropane. Data from the distillation of the saturated catalyzate ( $n_D^{20}$  1.3569;  $d_4^{20}$  0.6242) are presented in Table 5.

From a comparison of the data of Tables 4 and 5, it is seen that Fractions 1 and 2 contain n-pentane with a small amount of 2-methylbutane. Fractions 3 and 4 consist of pure n-pentane. The composition of the catalyzate is approximately the following: 87% n-pentane and 15% 2-methylbutane.

Hydrogenation of 1,1,2-Trimethylcyclopropane in the Presence of Platinized Carbon. 1,1,2-trimethylcyclopropane was passed at 150° and a space rate of 0.2 hours<sup>-1</sup> through a tube containing platinized carbon (20% Pt). The saturated catalyzate (3.8 g) had a b. p. of 50.1° (760 mm),  $n_D^{20}$  1.3685 and  $d_4^{20}$  0.6495; i. e., it was 2,2-dimethylbutane.

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\*Original Russian pagination. See C. B. Translation.



# ON THE QUESTION OF THE SYNTHESIS OF CYCLOPENTYL- AND CYCLOHEXYL-SUBSTITUTED MESITYLENES

E. S. Pokrovskaya and N. A. Shmanko

(Presented by Academician A. V. Topchlev, June 11, 1958)

As has been shown in a number of researches on the synthesis of alkylcycloalkylbenzenes, the introduction of a cyclopentyl or cyclohexyl group into an aromatic ring by reaction of cyclopentene or cyclohexene with aromatic hydrocarbons in the presence of anhydrous aluminum chloride proceeds smoothly and with good yield in many cases [1].

However, in the case of some alkylbenzenes, aluminum chloride causes isomerization of the original aromatic hydrocarbon.

Alkylation of mesitylene with cyclopentene gave trimethylcyclopentylbenzene (b. p., 100°/2 mm;  $n_D^{20}$  1.5330,  $d_4^{20}$  0.9424, glass freezing point, -45° [2]), which was obtained by us earlier. This hydrocarbon was later prepared by this same route by Cagniant et al, the authors citing for this compound a b. p. of 138-139°/15 mm,  $d_4^{20}$  0.943 and  $n_D^{20}$  1.5212 [3].

A comparatively uncomplicated and completely reliable method of establishing the position of substituents in monocyclic aromatic hydrocarbons with alkyl and cycloalkyl substituents is by spectral analysis using absorption spectra obtained in the near ultraviolet region [4-6]. In using this method, the better studied methylated benzenes can be used as standards of comparison.

The absorption spectrum in the near ultraviolet region of trimethylcyclopentylbenzene is shown as Figure 1, II\*. From the similarity of this spectrum to the spectrum of durene (Figure 1, I) and the sharp difference from the spectrum of isodurene (Figure 2, I), it can be concluded that in this trimethylcyclopentylbenzene, the substituents are in the 1, 2, 4, and 5 positions. Hence, it may be concluded that during the interaction of cyclopentene with mesitylene in the presence of aluminum chloride, isomerization of the mesitylene to 1,2,4-trimethylbenzene occurs, and the

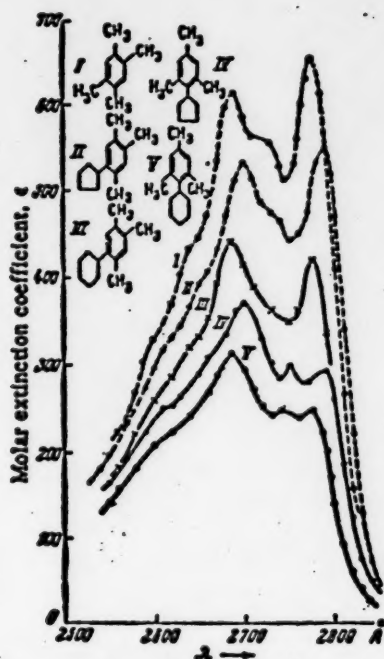


Fig. 1. Absorption spectra. I) durene [4], II) cyclopentylpseudodurene [5], III) cyclohexylpseudodurene [5], IV) cyclopentylmesitylene, V) cyclohexylmesitylene.

\* The absorption spectra of all of the hydrocarbons described in the present paper were investigated with the aid of an "Uvispek" photoelectric spectrophotometer with a quartz optical system and with special temperature control for the cell installed in the camera; this spectrophotometer is similar in action to the Beckmann and SF-4 spectrophotometers. The hydrocarbons were investigated in equimolar solutions (0.00250 and 0.00350 mole/liter in spectroscopically pure isooctane-2,2,4-trimethylpentane) at 20°.

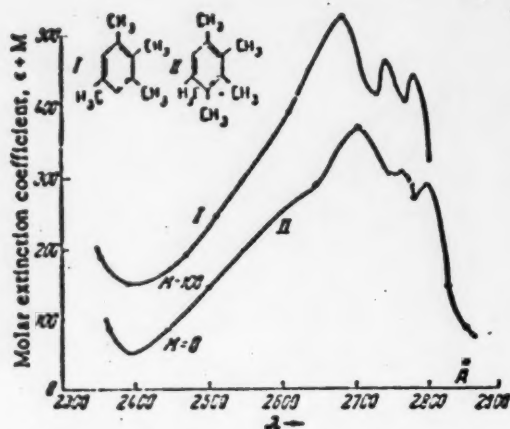


Fig. 2. Absorption spectra.  
I) isodurene [7], II) pentamethylbenzene [7].

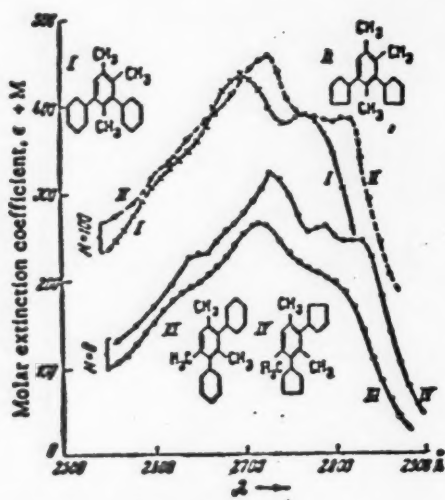


Fig. 3. Absorption spectra.  
I) dicyclohexylpseudocumene [5], II) dicyclopentylpseudocumene, III) dicyclohexylmesitylene, IV) dicyclopentylmesitylene

The residue, which boiled above 270° during distillation over metallic sodium, boiled in the range 155–160° at 3 mm. This product crystallized on standing. After several recrystallizations from ethyl alcohol, a white, crystalline substance with an m. p. of 63.7° was obtained. This solid hydrocarbon must have the structure dicyclopentylmesitylene or 1,3,5-trimethyl-2,4-dicyclopentylbenzene.

• The different natures of the substituent groups in trimethyldicyclopentylbenzene and pentamethylbenzene and their investigation in spectroscopic instruments of different resolving powers were apparent in the intensities of the maxima in the absorption spectra of these compounds.

cyclopentyl radical enters the ring in the 5 position. The trimethyldicyclopentylbenzene resulting from this same synthesis was a viscous liquid with a b. p. of 159–160°/3 mm,  $n_D^{20}$  1.5540, and which freezes to a glass at –10°.

The spectrum of this hydrocarbon is shown as Figure 3, II. As would be expected, this spectrum bears a marked similarity to the spectrum of pentamethylbenzene (Figure 2, II)\*. Though we did not have the opportunity to determine precisely the distribution of the substituents in the molecule of this aromatic hydrocarbon – trimethyldicyclopentylbenzene – we nevertheless consider the most probable structure to be 1,2,4-trimethyl-3,5-dicyclopentylbenzene.

With the aim of preparing cyclopentylmesitylene without isomerization of the initial material, we carried out the alkylation of mesitylene with cyclopentene in the presence of concentrated sulfuric acid.

The original mesitylene had the following properties, which are in agreement with the literature values for mesitylene [8]: b. p., 163.5°/740 mm,  $n_D^{20}$  1.4993 and  $d_4^{20}$  0.8651. The alkylation of mesitylene with cyclopentene was carried out with cooling in the presence of concentrated sulfuric acid.

A substance having the following properties was isolated from the reaction products: b. p., 100.5–101.5°/3 mm and 266–267°/755 mm;  $n_D^{20}$  1.5343,  $d_4^{20}$  0.9441, and m. p. –8.7°; the formula (by analysis) was  $C_{14}H_{18}$ . This hydrocarbon differed in physical properties from the above-described trimethyldicyclopentylbenzene with the durene type of structure.

The absorption spectrum in the near ultraviolet region of this hydrocarbon (Figure 1, IV) also differed sharply from the spectrum of the previously prepared trimethyldicyclopentylbenzene (Figure 1, II), and it bore considerable similarity to the spectrum of isodurene (Figure 2, I).

Hence, it follows that isomerization does not proceed during the condensation of mesitylene with cyclopentene in the presence of concentrated sulfuric acid, and the hydrocarbon synthesized was cyclopentylmesitylene (1,3,5-trimethyl-4-cyclopentylbenzene).

The absorption spectrum of this hydrocarbon in the near ultraviolet region is shown as Figure 3, IV. This spectrum differs little in outward appearance, in position, and in intensity from the absorption spectrum of 1,2,4-trimethyl-3,5-dicyclopentylbenzene (Figure 3, II).

With the aim of preparing cyclohexylmesitylene, we carried out the alkylation of mesitylene with cyclohexene in the presence of anhydrous aluminum chloride. The reaction mixture was cooled with ice.

A hydrocarbon having the following properties was isolated from the products of this reaction: b. p. 119-120°/2 mm;  $n_D^{20}$  1.5309,  $d_4^{20}$  0.9384, and f. p. to glass of -19°. The hydrocarbon previously prepared by Bodroux had b. p. 283-284°,  $n_D^{20}$  1.535 and  $d_4^{20}$  0.946 [9], which are close to our data.

A crystalline material with a m. p. of 148° was isolated from the higher reaction products; this hydrocarbon, which is not described in the literature, corresponds in composition to the formula  $C_{22}H_{22}$  (by analysis).

The considerable similarity which the spectrum of the liquid hydrocarbon in the near ultraviolet region (Figure 1, III) bears to the spectrum of durenene (Figure 1, I) indicates that the interaction of cyclohexene with mesitylene in the presence of anhydrous aluminum chloride, even with cooling, proceeds with isomerization of the mesitylene in complete analogy to this same reaction with cyclopentene.

The synthesized hydrocarbon is 1,2,4-trimethyl-5-cyclohexylbenzene.

Considering the structure established for the liquid hydrocarbon, the most probable structure for the solid hydrocarbon (m. p. 148°) is 1,2,4-trimethyl-3,5-dicyclohexylbenzene. The absorption spectrum of this hydrocarbon is shown as Figure 3, I.

With the aim of obtaining unisomerized reaction products, the condensation of mesitylene with cyclohexene was carried out in the presence of concentrated sulfuric acid at mole ratios of mesitylene: cyclohexene: sulfuric acid of 2:1:2; the reaction mixture was cooled with ice.

A substance with the following properties was isolated from the reaction products: b. p. 107-108°/2 mm.  $n_D^{20}$  1.5320,  $d_4^{20}$  0.9402, and f. p. 13.2 (crystalline). Its composition corresponded to the formula  $C_{15}H_{12}$  (by analysis).

This hydrocarbon differed in its properties from the previously described cyclohexylpseudomesitylene.

The spectrum of this compound (Figure 1, V) bore a great resemblance to the spectrum of cyclopentylmesitylene (Figure 1, IV). An isodurene type of structure was established above for the latter compound; hence, it follows that the structure of the synthesized compound corresponds to 1,3,5-trimethyl-2-cyclohexylbenzene.

Thus, isomerization does not proceed during the condensation of mesitylene with cyclohexene in the presence of concentrated sulfuric acid, which is in complete analogy with this same reaction for cyclopentene.

From the high-boiling fractions of the products of this reaction was isolated, by distillation over metallic sodium, a fraction boiling at ~180-185°/3 mm, which distilled as a viscous mass and which crystallized on standing. After several recrystallizations from alcohol, a substance was isolated which crystallized in the form of fine needles with a m. p. of 127.8°. The composition  $C_{22}H_{22}$  was found for this hydrocarbon (by analysis).

This solid hydrocarbon must have the structure dicyclohexylmesitylene or 1,3,5-trimethyl-2,4-dicyclohexylbenzene.

The absorption spectrum of this hydrocarbon is shown as Figure 3, III.

The melting points of cyclopentylmesitylene, dicyclopentylmesitylene, cyclohexylmesitylene, and dicyclohexylmesitylene were determined by a thermographic method by N. I. Lashkevich, for which we express our appreciation.

A. P. Bogomolova took part in the work.

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## INFRARED SPECTRA OF ORGANOLITHIUM COMPOUNDS. THE INTERMOLECULAR LITHIUM BOND

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AN SSSR K. A. Kocheshkov

The present work was devoted to an investigation of the infrared absorption spectra of organolithium compounds of the types  $\text{Alk-Li}$  and  $\text{Ar-Li}$ . The spectra investigated were those of methyl-, ethyl-, butyl-, dodecyl-, phenyl-, *p*- and *o*-tolyl-, and  $\alpha$ -naphthyllithium, which were prepared and purified by the method described in references [1, 2].

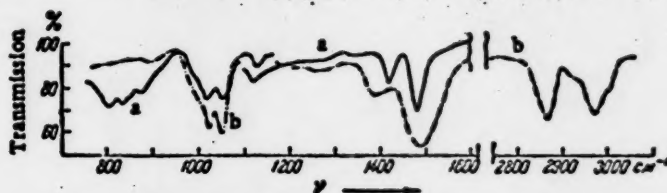


Fig. 1. I. r. spectra of crystalline (a) and vaporous (b) methylolithium. NaCl and LiF prisms.

In the spectrum of methylolithium (Figure 1), in agreement with the theory of vibrations of molecules of this type, six fundamental frequencies were observed, among which the band with a frequency of  $1052\text{ cm}^{-1}$  is assigned to the valence vibration of the  $\text{C-Li}$  group. Such assignment is in agreement with an analysis of the spectra of ethyl-, butyl-, and dodecyllithium. Thus, for this series of compounds, a valence vibration frequency of  $\sim 1050\text{ cm}^{-1}$  for the  $\text{C-Li}$  group is characteristic. The change in the intensity and location of this band in the spectra of crystals and solutions of organolithium compounds also supports this assignment. Thus, in the spectra of methyl- and ethyllithium powders in vaseline oil, in addition to the band with a frequency of  $1056\text{ cm}^{-1}$ , there is a new, intense band with a frequency of about  $880\text{ cm}^{-1}$ , which is absent in the spectra of the vapors. In the spectrum of concentrated solutions of ethyllithium in benzene, the intensity of the new band with maxima at  $\sim 925\text{ cm}^{-1}$  and  $880\text{ cm}^{-1}$  is significantly greater than the intensity of the band due to the free  $\text{C-Li}$  group. The change in the intensities of the bands at  $\sim 1050\text{ cm}^{-1}$  and those lying in the interval  $915\text{--}880\text{ cm}^{-1}$  are interconnected. The relative increase or decrease in the intensity of the band at  $\sim 1050\text{ cm}^{-1}$  is always accompanied by a decrease or increase in the intensities of the bands lying in the interval  $915\text{--}880\text{ cm}^{-1}$ . These facts provide clear confirmation of the correctness of the assignment of the band at  $1050\text{ cm}^{-1}$  to the valence vibrations of the  $\text{C-Li}$  group.

The change in the frequency of the valence vibration of the  $\text{C-Li}$  group upon transition from the vapor state to the solid and solution states is apparently connected with participation of the  $\text{C-Li}$  group in crystals and solutions in some kind of intermolecular interactions leading to a shift of the  $\text{C-Li}$  band toward the longer wave lengths.



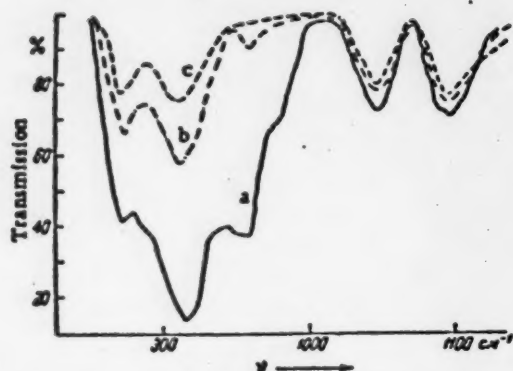


Fig. 2. I. r. spectra of ethyllithium in benzene at various concentrations. a) 0.9 N solution, b) 0.4 N solution, c) 0.23 N solution. NaCl prism,  $d = 0.3$  mm

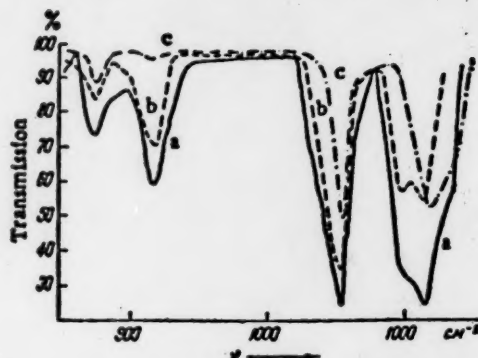


Fig. 3. I. r. spectra of solutions of ethyllithium in hexane at different concentrations. a) 0.6 N solution, b) 0.4 N solution, c) 0.27 N solution. NaCl prism,  $d = 0.1$  mm

Thus, the spectra show unequivocally that the molecules of organolithium compounds in crystals and in solutions are associated with the formation of complexes. This conclusion is in complete agreement with the work of other authors [3-6], who reported cryoscopic and ebullioscopic data supporting association of these compounds. Naturally, during a transition from the solid state to solution in non-polar solvents, the character of the association should change substantially.

If the existence of chains is possible in solutions in nonpolar solvents, the formation of aggregations with a decrease in the over-all dipole interaction is more favored; this can be realized through the formation of different rings and also by a change in the nature and length of the chains. Thus, in the spectra of freshly prepared solutions of ethyllithium in benzene, toluene, and *m*-xylene, the majority of the molecules are associated, with a predominance of one of the types of aggregates ( $926\text{ cm}^{-1}$ ). On dilution, the relative intensity of the band at  $926\text{ cm}^{-1}$  sharply decreases and those of the bands at  $875$ ,  $1050$ , and  $1100\text{ cm}^{-1}$  increase (Figure 2).

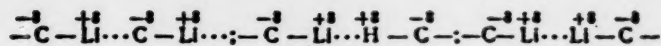
When a solution of ethyllithium in benzene is heated to  $70^\circ$  or when such a solution is allowed to stand in an atmosphere of nitrogen in the light, a similar change in the intensities of these bands is observed. It is possible that different types of aggregates actually exist in solution, and these types are converted one into another under the indicated conditions. Such a conclusion is in conformity with cryoscopic data, which give association factors of six [4, 7, 8] and two [6] for benzene solutions of ethyllithium. It can be assumed that the band at  $875\text{ cm}^{-1}$  belongs to the  $\text{C}-\text{Li}\dots$  group in dimers and the band at  $926\text{ cm}^{-1}$  is associated with this group in hexamers.

Investigation of the spectra of solutions of ethyllithium in hexane, cyclohexane, and cyclohexene (the ethyllithium was recrystallized from these same solvents) shows that the fraction of the molecules not participating in aggregates is greater than the fraction of associated molecules, and the nature of the aggregation in these solvents is different from that in aromatic hydrocarbons. Thus, in the spectra of solutions of ethyllithium in hexane and cyclohexane, the very intense bands of the free  $\text{C}-\text{Li}$  groups at about  $1050\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  and the bands at  $926\text{ cm}^{-1}$  and  $877\text{ cm}^{-1}$  appear only at higher concentrations, and their intensities drop with dilution of the solution (Figure 3). The nature and degree of association of  $\text{R}-\text{Li}$  molecules in a given solvent must depend considerably on the length of the hydrocarbon chain. With an increase in chain length, the probability of the formation of cyclic aggregates must decrease and that of the formation of linear complexes must increase. An exception is methylithium, in which the methyl group interferes with the formation of cyclic aggregates in solutions, and this apparently is explained by the insolubility of  $\text{CH}_3\text{Li}$  in hexane and benzene. It is obvious that a change in the nature and degree of association of  $\text{R}-\text{Li}$  molecules with changes in the nature of the compound, the solvent, the concentration, and the temperature must have a considerable effect on the dipole moment. Therefore, it may be assumed that the dipole moment of ethyllithium measured in dilute hexane solutions must approach the dipole moment of the free molecule. Measurements carried out by V. N. Vasil'eva together with us actually showed that in dilute solutions of ethyllithium in hexane,  $\mu \approx 1.1$  D, while the dipole moment of ethyllithium in

benzene is 0.77 D and does not change with dilution. The different behavior of ethyllithium in aliphatic and aromatic hydrocarbons can be explained on the basis that the energy of dispersive interaction is greater between cyclic aggregates and benzene molecules than between cyclic aggregates and hexane molecules owing to the greater polarizability of the molecules of the first solvent. The lower solubility of ethyllithium in hexane is apparently connected with this.

**Our data indicate that benzene does not take part directly in associations with ethyllithium.**

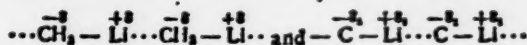
On the basis of all of the experimental data we have concluded that association of organolithium compounds by means of an intermolecular lithium bond occurs. Let us consider all possible cases of formation of this bond.



The first type of interaction is the most probable of the three possible cases, since the  $\overset{-\delta}{\text{C}}-\overset{+\delta}{\text{Li}}$  dipoles are lined up with opposite charges opposing each other. In the second and third cases the dipoles have similar charges opposed, and, therefore, these cases of interaction are less probable. If a lithium bond should exist between the C-Li group and a hydrogen atom, such interaction would be more favored with methyl group hydrogens, not only of the molecules of organolithium compounds but also of the solvent. If  $\text{C}-\text{Li} \cdots \text{H}-\text{C}$  interactions were present, changes in the bands of the  $\text{CH}_3$  group should be observed in the spectrum, and there should be no dependence of the intensity of the  $\text{C}-\text{Li} \cdots$  group on the concentration of the solvent. The experiments showed the reverse to be the case. Thus, there remains the single possible explanation of the association of organolithium compounds through the groups  $-\overset{-\delta}{\text{CH}_2}-\overset{+\delta}{\text{Li}}$  and  $\overset{-\delta_1}{\text{C}}-\overset{+\delta_1}{\text{Li}}$ .

An important condition providing for the formation of a lithium bond between  $-\overset{-\delta}{\text{CH}_2}-\overset{+\delta}{\text{Li}}\cdots\overset{-\delta}{\text{CH}_2}-\overset{+\delta}{\text{Li}}$  groups is the presence of dipole moments.

However, direct interaction between lithium and carbon atoms of two molecules,  $\overset{-\delta}{\text{C}}-\overset{+\delta}{\text{Li}} \cdots \overset{-\delta}{\text{C}}-\overset{+\delta}{\text{Li}}$ , is hindered by the screening due to the two hydrogen atoms bonded to the carbon. Apparently the lithium bond also occurs with some participation of hydrogen atoms of the methylene group. Such a supposition is in agreement with the fact that bands with frequencies in the region of 2750-2870  $\text{cm}^{-1}$ , which can be assigned to the group  $-\text{H}_2\text{C}-\text{Li} \cdots$  group taking part in association, are observed in the spectrum of ethyllithium. These frequencies are not observed in the spectrum of ethyllithium vapors. Thus, in our study of the infrared spectra of organolithium compounds, we observed and investigated the formation of intermolecular lithium bonds



A peculiarity of this bond is that the carbon atom participating in the formation of the bond does not have an "unshared" pair of electrons. Nevertheless, this bond is quite stable (the relative shift amounts to 17%).

The explanation of these facts must apparently be sought in the special nature of the lithium atom: the small radius, the significantly lower ionization potential, and the good possibility of using the p-orbital in comparison with the hydrogen atom.

Apparently, the nature of the forces causing association of molecules of organolithium compounds through the lithium bond do not differ in principle from the forces arising in the formation of hydrogen bonds in  $B_2H_6$  and  $R_2AlH$  molecules [9]. The formation of the lithium bond in  $\overset{-\delta}{CH_3}-\overset{+\delta}{Li} \cdots \overset{-\delta}{CH_3}-\overset{+\delta}{Li}$  systems can be understood from the point of view of the formation of molecular orbitals with the participation of valence electrons of  $CH_3-Li$  groups and also of dipole interaction between them.

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\*Original Russian pagination. See C. B. Translation.

# INVESTIGATION OF THE SYSTEM SnTe - GeTe

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(Presented by Academician I. P. Bardin, June 28, 1958)

In previous work [1, 2], we investigated the pseudobinary systems formed by semiconductor compounds with a structure of the type of NaCl: PbSe - PbTe and SnTe - PbTe; it was shown that continuous series of solid solutions are formed in both systems.

In the present work, the ternary system Sn - Ge - Te was investigated along the section SnTe - GeTe. Metallic properties appeared to a considerable degree in both compounds.

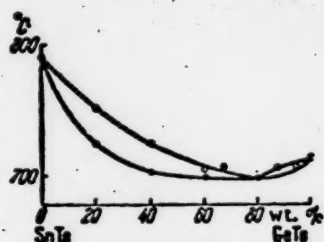


Fig. 1. Equilibrium diagram of the system SnTe - GeTe.

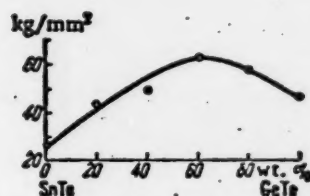


Fig. 2. Microhardness of the alloys.

TABLE 1

Lattice Constants of the Alloys

SnTe	GeTe	a, Å	$\alpha$
wt. %			
100	0	6.29	90°
80	20	6.24	89°40'
60	40	6.16	89°26'
40	60	6.10	88°58'
20	80	6.04	88°35'
1	100	5.94	88°22'

The equilibrium diagram of the system Sn - Te was investigated by Pelabon [3], Fay [4], Biltz and Mecklenburg [5], and Kobayashi [6]. There is one chemical compound in this system, SnTe, which melts with an open maximum at 790°. The heat of formation of the compound SnTe is 14.65 kcal/mole [7]. On the magnetic susceptibility isotherms of the liquid alloys there is a sharp minimum corresponding to the composition of the compound SnTe, which indicates that dissociation of this compound is very insignificant [8]. A region of solid solutions based on the compound SnTe was not observed. The compound SnTe has a structure of the NaCl type with a lattice constant of 6.285 Å [9]. According to our data [2], the electrical conductivity of SnTe is 8350 ohm<sup>-1</sup>·cm<sup>-1</sup>, and the

thermal electromotive force with respect to copper is 21  $\mu$ v/degree.

The equilibrium diagram of the system Ge - Te was worked out by Klemm and Frischmuth [10]. In this system, there is one chemical compound, GeTe, which melts peritectically at 725°. Schubert and Fricke [11] determined the crystal structure of the compound GeTe. At room temperature, this compound has a face-centered rhombohedral lattice with the parameters  $a = 5.962$  Å and  $\alpha = 88°21'$ . With an increase in temperature, this lattice



transforms to a face-centered cubic NaCl type with a constant of  $5.986 \text{ \AA}$  at  $460^\circ$  from the germanium-rich side and  $5.97 \text{ \AA}$  at  $390$  from the tellurium-rich side. This transition occurs gradually as the temperature is increased. This difference in transition temperature with a change in composition can be explained by the solubility of the components in the solid compound. In the opinion of the authors of reference [11], the limit of the region of solid solutions based on the compound  $\text{GeTe}$  is at a concentration of 50 atom % Te on the tellurium-rich side.

The equilibrium diagram of the system  $\text{Sn} - \text{Ge}$  is an eutectic type with the eutectic lying very close to pure tin. The eutectic melting point is  $232^\circ$  [12].

The starting materials for the present investigation were germanium with a resistivity of  $10 \text{ ohm} \cdot \text{cm}$ , grade 01 tin, and the second form of tellurium, which was purified by two-fold vacuum distillation and had a content of iron, silicon, aluminum, and magnesium of less than 0.01%. The samples for investigation were melted in evacuated sealed tubes. The liquid alloys were mixed by repeated shaking of the tube, and were then cooled in air. Annealing of the alloys was carried out at  $450^\circ$  for 320 hours for those samples used for the investigation of properties and at  $500^\circ$  for the samples for x-ray analysis. After annealing was complete, the tubes in which the alloys were sealed were taken from the furnace and cooled in air. The equilibrium state of the alloys was checked by an investigation of the microstructure. Sections were etched with dilute (1:1) nitric acid. This etchant imparts a dark color to  $\text{SnTe}$  and a lighter color to  $\text{GeTe}$ . Thermal analysis was carried out by recording the cooling curves of cast alloys and the heating curves of annealed alloys with a N. S. Kumakov pyrometer and a differential thermocouple. The standard was a 75%  $\text{PbSe}$  and 25%  $\text{PbTe}$  alloy which had been brought to equilibrium by lengthy annealing.

The x-ray photographs were taken with Debye cameras using iron radiation. The microhardness was measured on a PMT-2 apparatus at a load of 20 g. The investigation of the electrical conductivity and thermal electromotive force was carried out with a PPTV-1 potentiometer. The thermal electromotive force was measured with respect to copper.

The results of the thermal analysis are shown in Figure 1. The liquidus and solidus lines pass through a minimum at a concentration of about 80%  $\text{GeTe}$  and a temperature of  $700^\circ$ . All curves on the thermograms had a form typical of the crystallization of solid solutions. Investigation of the microstructure of the alloys showed that a continuous series of solid solutions was formed; the alloys, after annealing, were single phase and had a polyhedral, coarsely crystalline structure. In the cast, rapidly cooled alloys, the crystals, after etching of the sections, were colored irregularly owing to dendritic liquefaction.

The results of the thermal analysis and investigation of the microstructure were confirmed by x-ray analysis and a study of the properties of the alloys; the x-ray pictures of the annealed alloys showed a gradual transition from the face-centered cubic lattice of the compound  $\text{SnTe}$  to the face-centered rhombohedral lattice of the compound  $\text{GeTe}$ .

Table 1 presents the lattice constants of the alloys investigated.

The microhardness of the alloys changes with composition along a curve with a maximum (Figure 2). The electrical conductivity of the cast alloys changes along a curve with a minimum (Figure 3), and the thermal electromotive force of the cast and annealed alloys changes along a curve with a maximum (Figure 4). (The electrical conductivity of the annealed alloys was not measured due to the high brittleness of the alloys in the

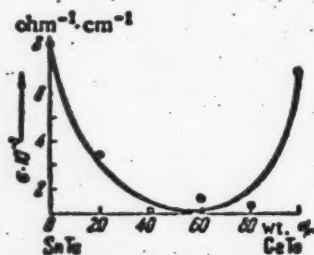


Fig. 3. Electrical conductivity of the alloys.



Fig. 4. Thermal electromotive force of the alloys.



central part of the system). The properties of the alloys are characteristic of a system in which a continuous series of solid solutions are formed.

This investigation of the system Sn-Ge-Te showed that, in this system, along the section between the two isostructural compounds SnTe and GeTe, there is formed a continuous series of solid solutions with a minimum on the melting diagram; the face-centered cubic lattice of the compound SnTe gradually changes to the face-centered rhombohedral lattice of the compound GeTe.

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## CONDENSATION TELOMERIZATION AND A NEW TYPE OF UNSATURATED POLYESTERS (POLYESTER ACRYLATES)

A. A. Berlin, G. L. Popova and E. F. Isaeva

(Presented by Academician A. V. Topchlev, June 25, 1958)

Investigations of the polymerization of dimethacrylate, allylmethacrylate, and carboxyallylmethacrylate esters of glycols have shown that with an increase in the distance between double bonds, the polymerization rate increases [1-2].

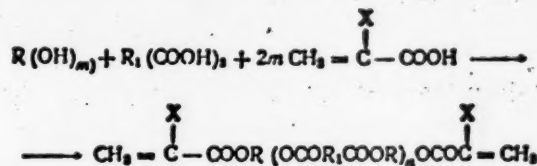
This peculiarity of di- and polyfunctional acrylates distinguishes them from the corresponding diethers and diesters of allyl and vinyl alcohols.

The possibility of obtaining highly active di- and polyfunctional monomers with a large number of "cross-linking" groups is of considerable theoretical and practical interest, since this would open up the possibilities: 1) of varying the flexibility of the cross links, 2) of regulating the contraction during the transition from monomer to trimer to polymer, and 3) of obtaining thermally stable polymeric products with a wide range of physico-mechanical properties.

In synthesizing such substances, we made use of the principle of regulation of chain growth during polyesterification of dibasic acids with glycols and glycerin by the addition of methacrylic (or acrylic) acid. This method of preparing comparatively low molecular-weight compounds with a given type of terminal functional groups may be considered as an instance of telomerization occurring by a condensation mechanism ("condensation telomerization").

The mechanism of reactions of this type has still not been studied, although there are indications that acid hydrolysis occurs during polyesterification leading to a decrease in the polydispersion and  $M_{av}$  when saturated monobasic acids are added during polyesterification of dicarboxylic acids with glycols [3, 4].

In its over-all form, the process of forming polyesters with terminal methacrylate (or acrylate) groups, which we call "polyester acrylates", can be represented by the scheme



The condensation telomerization was carried out in inert solvents (benzene or toluene), the water formed being removed by azeotropic distillation.

Phosphoric, sulfuric, ethylsulfuric, and p-toluene-sulfonic acids were used as catalysts.

The highest reaction rate (process time of 8-12 hours) and the highest yields of polyester acrylates (85-95% of theoretical based on the dibasic acid) were obtained using 2-3% sulfuric or p-toluene-sulfonic acid in the presence of 0.5-0.8% hydroquinone.

TABLE 1

## Physicochemical Properties of Polyester Acrylates

Expt. No.	Name of compound (according to average formula)	Viscosity at 20°, cp	$M_{av}$		$n_D^{20}$ , g/cc	AR		Bromine number		Ester number		Notes
			Found	Calc.		Found	Calc.	Found	Calc.	Found	Calc.	
1	Dimethacrylate-bis-ethylene-glycol phthalate	40	350	300	1.5000	97.29	90.94	80.0	82	570.0	575.0	No free OH groups were detected in any of the polyester acrylates
2	Dimethacrylate-bis-ethylene-glycol phthalate	20-60 125	305	478	1.4930	119.20	118.64	63.0	64	470.0	488.6	
3	Dimethacrylate-bis-triethylene-glycol phthalate	100-150 125	520	566	1.4891	140.50	140.46	60.0	58.5	393.0	395.7	Acid numbers of the purified polyester acrylates were close to 0.0
4	Dimethacrylate-bis-ethylene-glycol sebacate	100-150 200	580	602	1.4660	152.30	153.39	50.0	53.1	336.0	372.0	
5	Tetramethacrylate-bis-glycerin phthalate	100-300 4000	591	586	1.4890	143.30	135.47	72.0	122.8	550.0	573.0	
6	Tetramethacrylate-bis-glycerin sebacate	3000-5000 4000	—	622	1.4870	148.0	158.40	60	102.8	535	540	

Under the conditions used, the degree of polymerization of the polyester acrylates depends mainly on the component ratios, primarily on the amount of methacrylic (or acrylic) acid.

For calculating the degree of polymerization to a first approximation, we used the simple relationship developed for similar polyesters:  $n = 2L/B$ , where  $L$  is the number of moles of dibasic acid, and  $B$  is the number of moles of monobasic acid.

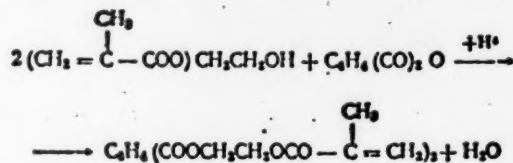
On the basis of this equation, with a ratio of 1 mole of dibasic acid to 2 moles of glycol to 2 moles of methacrylic acid, the formation of polyester acrylates with  $n = 1$  would be expected. When glycerin is used, a monomeric product should be obtained when 4.0 moles of monobasic acid are used.

A decrease in the amount of methacrylic acid to 0.5-0.1 mole led to higher polymeric products ( $n \approx 4$ ). After the polyesters had been distilled, washed, and dried, they were freed from tarry impurities by means of activated aluminum oxide.

Attempts to fractionate the polyesters at pressures down to  $10^{-5}$  mm were unsuccessful owing to their low volatility and very great tendency to polymerize.

The molecular weights, determined cryoscopically, the molar refractions, bromine and ester numbers, elemental analyses, and hydroxyl group contents indicate that the major part of the products consisted of polyesters for which  $n$  corresponded to the calculated value (see Table 1).

This conclusion is confirmed by the fact that dimethacrylate-(bis-ethyleneglycol) phthalate synthesized from the methacrylic acid ester of ethylene glycol according to the reaction:



was practically indistinguishable from the corresponding compound synthesized by condensation telomerization at  $L/B = 1/2$  (see Table 2).

The polyester acrylates described in the present paper will find ever-increasing use for the production of various polymeric materials.

TABLE 2

Comparison of the Physicochemical Properties of Dimethacrylate-(bis-ethyleneglycol) Phthalates Prepared by Single and Two-Stage Methods

	Elemental composition, %			Ester number	Bromine number	$d_4^{20}$	$n_D^{20}$	$M_{av}$	MR
	C	H	O						
Calculated data	61,53	5,64	32,83	575	82,0	—	—	390	96,64
Single stage method of synthesis	61,50	5,50	32,85	570	80,0	1,18	1,500	350	97,20
Two-stage method of synthesis	—	—	—	572	80,2	1,18	1,500	—	97,20

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# FERMENTATIVE SYNTHESIS OF OPTICALLY ACTIVE PEPTIDES FROM GLYCOLIC ESTERS OF D,L-AMINO ACIDS

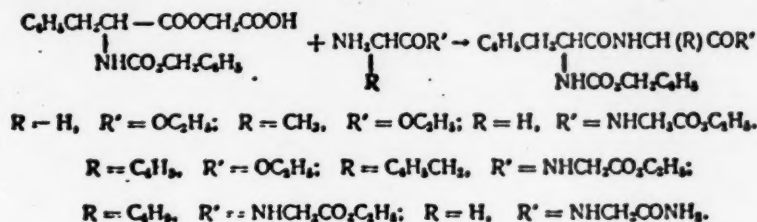
M. M. Botvinik and V. I. Ostoslavskaya

(Presented by Academician A. N. Nesmelanov, May 8, 1958)

It was recently shown by one of us [1] that esters of benzoylphenylalanine and  $\beta$ -hydroxyamino acid esters formed at the hydroxyl group of the hydroxyamino acid, the so-called O-peptides, can react with esters of amino acids and peptides in the presence of chymotrypsin with the formation of new optically active N-peptides. The reaction proceeds selectively, which results in the formation of optically active peptides.

Such reactions can be used for the synthesis of relatively scarce peptides. However, the use of O-peptides of serine in this reaction is not advantageous, and the ethyl esters of acylated amino acids react very poorly. Therefore, the present work was devoted to a study of the feasibility of using the available esters of hydroxy acids — glycolic and lactic.

The acylamino acid donors used were glycolic and lactic acid esters — hippurylglycolic, benzoyl-D, L-phenylalanylglycolic, benzoyl-D,L-phenylalanylactic, and carbobenzyloxy-D, L-phenylalanylglycolic acids. The acceptors were the ethyl esters of glycine, L- and D,L-leucine, L- and D,L-phenylalanylglycine, L- and D,L-leucylglycine and the ester and amide of glycyglycine. Esters or amides of acylated N-peptides or L-phenylalanine were formed in all cases.



In those cases where the acceptors were optically active esters of amino acids or peptides, the corresponding optically active L,L-peptides were obtained; if the acceptors were esters of racemic amino acids or peptides, the major portion of the resulting product was the same L,L-peptide, as was shown by the similar values of the specific rotation and the absence of a depression of the mixed melting point.

The carbobenzyloxy group was removed by hydrogenation from one of the esters of carbobenzyloxy dipeptides, and the resulting hydrochloride of the dipeptide ester was introduced into the reaction as an acceptor. In this manner was obtained the ethyl ester of carbobenzyloxy-L-phenylalanyl-L-phenylalanylglycine.

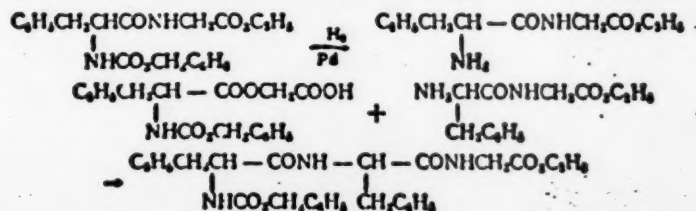


TABLE 1

The Interaction of Glycolic and Lactic Esters of Acylated Amino Acids with Esters of Amino Acids and Peptides

Experiment No.	Donor	Weight, g	Acceptor	Weight, g	D/A, mole	Time, hours
1	O-benzoyl-D,L-phenylalanylglycolic acid	0.2	Hydrochloride of the ethyl ester of:	0.3	1:3.5	1
2	O-benzoyl-D,L-phenylalanyllactic acid	0.1	glycine	0.15	1:3.5	1
3	O-carbobenzoyloxy-D,L-phenylalanylglycolic acid	2.1	glycine	3	1:3.7	24
4	The same	0.49	D,L-leucine	1.6	1:4	24
5	The same	0.22	L-leucine	0.6	1:3	2
6	The same	0.28	D,L-phenylalanylglycine	0.75	1:5	24
7	The same	0.22	L-phenylalanylglycine	from 0.55 g CBZ*	1:2.5	24
8	The same	0.28	D,L-leucylglycine	0.7	1:3	24
9	The same	0.14	L-leucylglycine	0.3	1:3	1
10	The same	0.47	glycylglycine	0.7	1:3	24
11	The same	0.21	Amide of glycylglycine	0.4	1:4	
12	Hippurylglycolic acid	0.2	Hydrochloride of ethyl ester of glycine	1.05	1:7	24

\*CBZ - carbobenzoyloxy

It is possible to extend this reaction to the synthesis of peptides of greater chain length. The yields of esters of carbobenzoyloxy peptides was 30-60% calculated on the L-antipode. Since, in the majority of cases, the material was precipitated from the reaction solution, their purification did not present any special difficulty.

Preliminary experiments showed that it is not necessary to use crystalline chymotrypsin in carrying out this reaction; it can be carried out with an extract from the pancreas.

1. Synthesis of O-benzoylphenylalanylglycolic acid. 2-Phenyl-4-benzyl-5-oxazolone (from 3 g of benzoylphenylalanine) was refluxed on a water bath for about 4 hours with 1.2 g of glycolic acid in ether-dioxane solution. The solution was evaporated under vacuum, and the oil which separated was dissolved in absolute benzene. The insoluble glycolic acid was filtered, and the solution was again evaporated to a light yellow oil, which crystallized when worked with water. The yield was 3 g, 83%; m. p. 79-80° (from alcohol).

Found %: C 66.03; 66.14; H 5.28; 5.37  
 $C_{18}H_{17}O_3N$ . Calculated %: C 66.05; H 5.19

2. Synthesis of O-benzoylphenylalanyllactic acid. 2-Phenyl-4-benzyl-5-oxazolone (from 3 g of benzoylphenylalanine) was refluxed 1 hour with 2 g of lactic acid in ether solution and allowed to stand for 18 hours. The ether was distilled under vacuum, and the remaining oil was washed with water. The residue was dissolved in alcohol, and the O-benzoylphenylalanyllactic acid was precipitated with water. The yield was 3 g, 80%; m. p. 160-162°.

Found %: C 66.81; 66.71; H 5.60; 5.78; N 4.21; 4.16  
 $C_{20}H_{19}O_4N$ . Calculated %: C 66.86; H 5.57; N 4.105

3. Synthesis of O-(carbobenzoyloxyphenylalanyl) glycolic acid. a) 5 g of carbobenzoyloxyphenylalanine in chloroform was treated with 2.4 ml of triethylamine; the mixture was cooled to -10°, and 1.6 ml of ethyl chlorocarbonate was added. After 10 minutes, a cooled chloroform solution of 2.5 g of glycolic acid and 4 ml of

TABLE 2

Amides and Esters of Carbobenzyloxy Peptides

Expt. No.	Compound	Yield		M. p. °C	Analysis, %		[ $\alpha$ ] <sub>D</sub> <sup>21-22</sup>
		%	mg		Found	Calc.	
3	Ethyl ester of carbobenzyloxy-L-phenylalanyl-glycine	58	650	109	—	—	—25.78** (C = 1.3%, alcohol)
4	L-leucine	32	100	114-115 <sup>(1)</sup>	C 68.43 H 6.50 N 7.57	C 68.18 H 6.36 N 7.27	—30.54* (C = 0.7%, alcohol)
5	L-leucine	34	46	114-115 <sup>(1)</sup>	—	—	—32.07* (C = 2%, alcohol)
6	L-phenylalanylglycine	54	110	184.5— 185.5 <sup>(2)</sup>	C 67.89 H 6.42 N 7.92	C 67.70 H 6.21 N 7.909	—25.62* (C = 1.4%, dioxane)
7	L-phenylalanylglycine	30	50	185.5-186	—	—	—26.05* (C = 0.6%, dioxane)
8	L-leucylglycine	48	41	154-155	C 65.01 H 7.16 N 8.51	C 65.19 H 7.04 N 8.45	—28.00* (C = 1.4%, alcohol)
9	L-leucylglycine	57	55	154-155	—	—	—26.68* (C = 1.85%, alcohol)
10	glycylglycine (isolated as the amide)	30	80	196-197	C 61.14 H 6.15 N 13.59	C 61.16 H 5.83 N 13.59	+10.31* (C = 0.7%, methyl alcohol)
11	Amide of L-phenylalanyl-glycylglycine	21	25	196-197	Amide 3.44	Amide 3.39	—
12	Ethyl ester of hippurylglycylglycine	0.5	10	173	—	—	—
1	Ethyl ester of benzoyl-L-phenylalanylglycine	19	20	146-148	—	—	—
2	Same	18	10	146-147	—	—	—

\*Lit. data: [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 17.3 + 0.5° (C = 2%, alcohol)<sup>(3)</sup> [ $\alpha$ ]<sub>D</sub><sup>25</sup> - 16.6° (C = 2%, alcohol)<sup>(4)</sup>; [ $\alpha$ ]<sub>D</sub><sup>21.5</sup> - 38.5° (C = 0.64%, alcohol) [ $\alpha$ ]<sub>D</sub><sup>21</sup> - 34° (C = 1.25%, alcohol)<sup>(5)</sup>.

triethylamine was added to the solution, and the mixture was allowed to stand for a day at 20°. The solution was then washed with 2 N HCl and water, and was then evaporated; the residue contained an oil which, along with the O-carbobenzyloxyphenylalanylglycolic acid, contained some unknown neutral substance. For removal of the impurity, the oil was again dissolved in chloroform, and was treated with a 1 N solution of soda. For better separation of the layers, ether was added. The soda solution was rapidly acidified with 2 N HCl, the oil which separated was extracted with chloroform, and the chloroform solution was evaporated under vacuum. Numerous attempts to crystallize the resulting oil were unsuccessful. Equivalent: found, 384, 400; calculated, 357.

**Saponification of the ester bond.** 0.0260- and 0.0209-g samples were back-titrated in alcohol solution, and each of the resulting solutions was added to 10 ml portions of 0.01 N NaOH; the solutions were boiled for 1 hour on a water bath, 10 ml of 0.01 N H<sub>2</sub>SO<sub>4</sub> was added, and the solutions were back-titrated. 5.4 and 4 ml, respectively, of 0.01 N NaOH were required to titrate the resulting carbobenzyloxyphenylalanylglycolic acid. Consequently, the oil contained 80% carbobenzyloxyphenylalanylglycolic acid.

b) 2.5 g of carbobenzyloxyphenylalanine and 1.3 ml of triethylamine in 15 ml of tetrahydrofuran were cooled to -10°, and immediately 0.8 ml of ethyl chlorocarbonate was added. This was allowed to stand 10 minutes in the cold, and 2.8 ml of triethylamine and then immediately 1.2 g of dry glycolic acid were added. CO<sub>2</sub> was evolved. The mixture was allowed to stand for another 5 minutes in the freezing mixture and then overnight at -20°. The mixture was partially evaporated and washed repeatedly with ether. The insoluble remainder was acidified and again extracted with ether. The ether extracts were washed with water and evaporated. The residue contained a colorless oil. The yield of carbobenzyloxyphenylalanylglycolic acid was 2.1 g. Equivalent: found, 372, 367; calculated, 357.



Saponification of the ester bond. 0.0239- and 0.0256-g samples of the material were back-titrated in alcoholic solution, and the resulting solutions were added to 9.472 ml of 0.01 N NaOH; these mixtures were boiled for an hour on a water bath. 5 ml of 0.01 N  $H_2SO_4$  was added, and the mixtures were back-titrated. 4.68 and 5.3 ml, respectively, of 0.01 N NaOH were required to titrate the carbobenzyloxyphenylalanine. Consequently, the oil contained 72-76% carbobenzyloxyphenylalanylglycolic acid.

Ammonolysis. 0.1718 g of the material was treated with 5 ml of a 25% solution of ammonia; after 1.5 hours, the precipitate was filtered. The yield of the amide of carbobenzyloxyphenylalanylglycolic acid was 0.102 g, which corresponds to a 75% content of O-carbobenzyloxyphenylalanylglycolic acid in the oil. M. p. 181°.

Found %: C 68.23; H 6.14; N 9.48  
 $C_{17}H_{19}O_3N_2$ . Calculated %: C 68.45; H 6.04; N 9.39

4. Synthesis of the hydrochloride of the ethyl ester of L-phenylalanylglycine. The hydrochloride of the ethyl ester of L-phenylalanylglycine was obtained in quantitative yield by hydrogenation of the ethyl ester of carbobenzyloxy-L-phenylalanylglycine over Pd/C in alcoholic hydrochloric acid solution. M. p. 139° (from alcohol-ether solution).

Found %: Cl 12.84;  $NH_2/N$  4.82  
 $C_{15}H_{19}O_3N_2Cl$ . Calculated %: Cl 12.56;  $NH_2/N$  5.13

The hydrochloride of the ethyl ester of L-leucylglycine and the hydrochloride of the amide of glycylglycine were prepared similarly.

5. Synthesis of optically active peptides. A weighed portion of the glycolic or lactic ester of the acylated amino acid mixed with the hydrochloride of the ester of the amino acid or peptide was dissolved in the minimum amount of alcohol, neutralized with 1 N NaOH, and 2 ml of phosphate buffer, pH 8, was added. The pH of the solution was then reduced to 7.8-8.2 (checked with an LP-4 potentiometer), and 1-1.5 g of the enzyme was added. The temperature of the reaction mixture was ~20°. After 5-15 minutes, the peptide began to precipitate. After the time indicated in Table 1, the precipitate was filtered, washed with 1 N HCl to the disappearance of a ninhydrin reaction and with a soda solution to the disappearance of a reaction with KI and  $KIO_3$  + starch, and was recrystallized from aqueous alcohol. If a precipitate did not form during the reaction, the entire solution was evaporated under vacuum, and the residue was treated with chloroform or ethyl acetate, washed with 1 N HCl, water, and soda, and evaporated. The reaction conditions and the results obtained are presented in Tables 1 and 2.

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## PREPARATION OF AND INVESTIGATION OF THE PHYSICOCHEMICAL PROPERTIES OF FRACTIONS OF CARBOXYMETHYLCELLULOSE

K. F. Zhigach, M. Z. Finkel'shtein, I. M. Timokhin and A. I. Malinina

(Presented by Academician A. V. Topchlev, July 3, 1958)

In recent years, water solutions of the sodium salt of the carboxymethyl ester of cellulose (carboxymethylcellulose — CMC) have found widespread practical application.

CMC is used in various fields of engineering as a stabilizer, emulsifier, adhesive, an additive to synthetic detergents, and for many other purposes [1, 2].

Carboxymethylcellulose is a complex polydisperse product consisting of various fractions differing from each other in chemical composition [3] and physicochemical properties, and it can be prepared in different degrees of esterification and polymerization.

Therefore, not just any grade can meet the requirements for a specific purpose. Of all the many possible CMC compounds, only specific ones are suitable for application in one field of engineering or another. The selection of the most effective grade of CMC in each individual case is made on the basis of experimental data, since up to the present a connection has not been established between the chemical composition of CMC samples and their physicochemical properties and the behavior of the same sample in a practical process.

Moreover, CMC samples almost always contain a certain amount of difficultly soluble swollen fibers, the so-called gel phase. Gel content can have a substantial effect on the properties of carboxymethylcellulose solutions.

According to the data of Dürig and Banderet [4], two types of CMC with the same average degree of substitution and degree of polymerization but with different gel contents have completely different rheological properties.

In connection with the above, the present work was devoted to the problem of studying the fractional composition of carboxymethylcellulose, the physicochemical properties of the fractions, and the effect of the various fractions on the behavior of CMC in practical use.

Four samples of CMC were selected for investigation; of these, the first was a grade used at the present time for stabilization of clay suspensions for drilling muds [2, 5], the second is used for stabilization of silicate-salt solutions when drilling wells through easily wetted and caving formations [2] and also as a cementing agent [6], the third, the German VHR grade, is also used in a number of countries for stabilization of drilling muds for oil wells, and the fourth was a specially prepared low-viscosity CMC product.

Fractionation of the samples was carried out as follows. To a 5-6% aqueous solution of the technical product at room temperature a precipitant — acetone or methanol — was added, slowly and with vigorous stirring, to the appearance of a stable suspension. The precipitated fraction was separated from the mother liquor by fractionation in a Büchner funnel or by centrifugation at 20,000 rpm, and was then freed from sodium chloride and sodium hydroxide by extraction with methanol.

Successive fractions were separated from the mother liquor in a similar manner.

In addition to fractionation by precipitation with alcohol, all samples, except the last, were separated into

the gel and sol phases by centrifugation of 2-3.5% aqueous solutions of the technical CMC products. The resulting gel and sol phases were treated with methanol or acetone and freed from alkali and sodium chloride. Some of them were subjected to fractionation by precipitation by the above method. The yields of the fractions were determined in per cents of the total weight of all fractions of the given sample. For these fractions, the degree of polymerization was determined by the method of Wurcz [7], and the degree of substitution was determined by iodometric determination of the copper in the copper salt of the carboxymethylcellulose.

The viscosity of the resulting CMC fractions was studied as well as their stabilizing effect on suspensions of the bentonitic clay askangel.

Preliminary investigations established that the viscosity of aqueous CMC solutions of 0.1% and higher concentrations do not follow Newton's law. Therefore, the present work was confined to investigations of dilute solutions (0.05%) in which, as shown by our determinations, there were practically no viscosity anomalies. The viscosity was determined with a Pinkevich\* viscosimeter at  $20 \pm 0.02^\circ$ .

The stabilizing effect of the CMC fractions was determined by filtration analysis with a pressure drop of 1 atm. 5% clay suspensions were used, with 10% NaCl added as a coagulant and 0.75% CMC fraction added as a stabilizer.

The amount of filtrate passing in 30 minutes through a filter paper of 60 sq. cm. area was measured.

TABLE 1

Sample No.	Fraction	Yield of fraction, wt. %	Viscosity of 0.05% solution, centipoises	Deg. of polymerization	Degree of esterification	Water loss, ml
1	Initial sample		2.4	354	85.1	5.5
	I Fraction	49.8	2.9	417	80.7	4.1
	II Fraction	32.5	2.5	391	83.6	3.9
	III Fraction	17.7	1.3	197	90.5	7.4
	Gel phase	5.0	3.6	518	76.0	7.4
	Sol phase	95.0	2.4	375	84.1	3.9
	I Fraction	56.1	2.5	404	80.6	4.0
2	II Fraction	43.9	2.3	342	86.0	3.9
	Initial sample		3.2	500	63.8	11.7
	Gel phase	19.30	7.1	635	58.9	26.0
	Sol phase	80.70	2.0	276	66.3	9.9
	I Fraction	66.50	2.0	280	64.9	10.1
	II Fraction	33.50	1.8	253	68.1	8.7
	III Fraction				79.3	5.0
3	Initial sample					51.2
	Gel phase	24.6				4.8
	Sol phase	75.4	4.2	547	84.1	5.2
	I Fraction	29.55	4.3	585	78.2	4.3
	II Fraction	70.45	3.6	512	91.9	—
	III Fraction				84.2	—
	IV Fraction				78.2	—
4	Water loss, ml			83		—
	I Fraction	82.9	—	92	78.2	—
	II Fraction	3.2	—	55	85.7	—
	III Fraction	4.5	—	54	85.7	—
	IV Fraction	5.2	—	44	102.5	—

The results obtained are presented in Table 1.

As seen from these data, the fractionation technique permitted us to develop the inhomogeneity of CMC with respect to both indices — both the degree of polymerization and the degree of esterification. In addition, a regular change in the composition of the fractions in the order of their separation was observed; fractions with a lower degree of polymerization were characterized by a higher degree of esterification, as shown in all of the samples studied.

Moreover, the study of CMC fractions separated by precipitation showed that they are not equal with respect to their stabilizing power. The third fraction of Sample No. 1, characterized by a low degree of polymerization, gave the highest water loss.

\* Translation of Russian — Publisher's note.

The present investigation also showed that the gel separated from CMC has little stabilizing effect. This is particularly apparent in Samples Nos. 2 and 3, for which the water loss was 26 and 51 ml, while the sol phase of these same samples lowered the water loss to 10 and 5 ml,

These data permit the conclusion that in determining the stabilizing effectiveness of CMC preparations not only by the degrees of polymerization and esterification [2, 5], but also the gel content should be considered.

The ratio of gel and sol phases in the product is significant not only when CMC is used as a stabilizer for clay suspensions, but also when it is used for other practical purposes, particularly during use as a cementing agent.

However, in this case the gel phase is the most effective, as we have shown experimentally by an investigation of the fractions of Sample No. 2.

Our comparative study of the degree of homogeneity of CMC and the properties of its separate fractions permits planning of routes for developing the most effective grades of CMC for a specific application.

I. M. Gubkin Moscow Petroleum Institute

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## ROUTE OF THE FORMATION OF PROPYLENE AND ETHYLENE DURING ISOBUTYLENE CRACKING

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Corresponding Member AN SSSR V. V. Voevodskii

It is known that during thermal decomposition of isobutylene, up to 50% of the material is converted to liquid (olefins, aromatic compounds) [1]. The first stage in the formation of liquid is apparently polymerization of the original olefin to dimers and trimers. The latter can undergo various transformations themselves at the usual cracking temperatures (500-700°) with the formation, finally, of liquid cracking products.

The carbon-hydrogen ratio of the products of the thermal cracking of isobutylene is approximately unity [2], while the ratio in isobutylene is two. Hence, it may be assumed that during the formation of liquids, hydrogen and methane are given off into the gas phase; in principle, partial formation of heavier gaseous cracked products containing 2 and 3 carbon atoms per molecule is possible. The question of what gaseous products are formed from the liquids or in the process of their formation and in what amounts the gases are formed has not been thoroughly studied.

The aim of the present work was the clarification of the route by which propylene — one of the main gaseous products of isobutylene cracking — is formed. A priori it may be expected that if propylene is formed only from isobutylene, the rate of its formation must vary with time in a manner opposite to that in which the rate of isobutylene consumption varies; i. e., it must decrease with time. If propylene is formed not from isobutylene, but from the liquid or from any of the low-stability intermediate products (but not from radicals), the rate of its formation must be zero at the beginning of the reaction and must then increase in conformity with the law of successive reactions. If propylene is formed by both routes, these pictures are superimposed. This is actually what occurred during our experiments.

We studied the rate of formation of propylene during isobutylene cracking by means of the isotope kinetic method [3]. In using this method, a small amount of labeled propylene was added to the isobutylene, and the concentration and specific activity of propylene was determined during the reaction. The labeled propylene was prepared by dehydration (at 370° over silica-alumina catalyst) of n-propyl alcohol labeled with carbon ( $C^{14}$ ) at the hydroxyl group\*. Cracking of a mixture of this propylene (15 mm Hg) and isobutylene (285 mm Hg) was carried out in a static vacuum system at 542°. The course of the specific activity,  $\alpha$ , and the concentration of propylene [ $C_3H_6$ ], are shown in Figure 1. The rate of formation of propylene  $\omega_1$ , calculated from the equation,

$$\omega_1 = -2,3 [C_3H_6] d \lg \alpha / dt,$$

is shown in Figure 2.

Values of the derivative  $d \lg \alpha / dt$  and concentration [ $C_3H_6$ ] were taken from the smoothed curves of Figure 1.

It is seen that at the beginning of the reaction, the rate  $\omega_1$  is not zero and that it increases over the course of 10-12 minutes, i. e., up to approximately 20% isobutylene conversion.

The increase in  $\omega_1$  indicates that an appreciable amount of the propylene formed during isobutylene cracking is not formed from isobutylene but from some of the intermediate products, evidently from the liquid. At the

\*E. D. Fedorov took part in the synthesis of the labeled propylene.

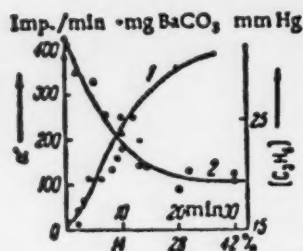


Fig. 1. Variation in concentration (1) and specific activity (2) of propylene with time. The numbers below the abscissa indicate per cent isobutylene conversion.

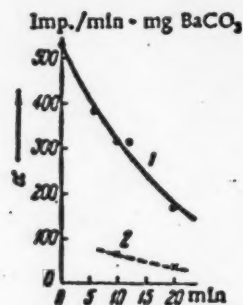


Fig. 3. Variation in specific activity of propylene (1) and of ethylene (2) with time.

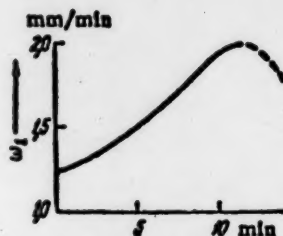


Fig. 2. Variation in rate of formation of propylene,  $\omega_1$ , with time.

time  $t = 0$ , there are no intermediate products, and the over-all rate of formation of propylene at this moment,  $\omega_1^0$ , is equal to the rate of formation of propylene from isobutylene. The difference  $\omega_1 - \omega_1^0$  is a measure of the rate of formation of propylene from intermediate products.

It must be remembered that the rate of isobutylene consumption is approximately constant up to 20-30% conversion [4].

As seen from Figure 2, in the region of 10-14 minutes the rate of propylene formation passes through a maximum and begins to decrease. Since the maximum lies in the region of high per cent conversion where the reaction is complicated by a number of side reactions, we consider that it is premature to form any quantitative conclusions from this fact.

In several experiments, in addition to the specific activity of propylene, the activity of ethylene was determined. The results of these experiments are shown in Figure 3. In order to interpret these results, it is necessary to know the ratio of the specific activity of the propylene to that of the ethylene formed from it.

Special experiments on the cracking of the labeled propylene used in our work ( $T = 600^\circ$ ,  $p_0 = 300$  mm Hg) showed that in the interval of from 14 to 45% conversion, the resulting ethylene had the same activity, calculated per carbon atom, as the initial propylene\*.

As seen from Figure 3, the activity of the ethylene in the experiments on isobutylene cracking was considerably lower than the activity of the propylene over the entire interval of isobutylene conversion.

This means that only part of the ethylene was formed from propylene. There are two possible routes of ethylene formation — directly from isobutylene or from the liquid.

On the basis of our experimental data, it is impossible to decide which of these routes predominates. That propylene can be formed from the liquid indicates that the formation of ethylene from the liquid is possible.

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Received July 28, 1958

\* This interesting result can evidently be explained only by assuming that during the catalytic dehydration of the *n*-propyl alcohol, the  $C^{14}$  tag in the resulting propylene was uniformly distributed along the carbon chain. There is no basis for thinking that in the original alcohol the tag was already uniformly distributed along the chain; however, we made no special effort to verify this.

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## THE PLUMBINATION REACTION

E. M. Panov and Corresponding Member AN SSSR K. A. Kocheshkov

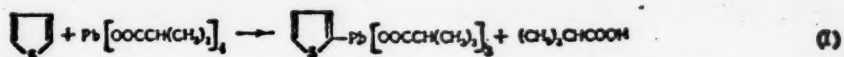
In spite of the fact that the direct introduction of metal atoms into an organic molecule by the action of metal salts has long been known (mercuration [1]) and that other reactions of this type have recently been discovered ("auration" [2] and "thallation" [3]), a direct "plumbination" reaction is presently not known.

As shown by Dimroth for mercuration and by one of us together with V. P. Glushkova [4], metal salts of organic acids can be successfully used for reactions of this type. On the other hand, it is known that thiophene undergoes mercuration particularly readily. All of this impelled us to carry out an investigation of plumbination based on reactions between tetravalent lead salts of organic acids and thiophene.

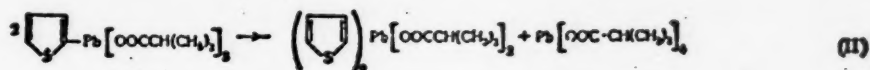
During our development of new methods of synthesis of organolead compounds [5], including those of the new class  $ArPbX_2$ , it was found particularly convenient to use lead tetraisobutyrate, which crystallizes well, is quite stable, and is soluble in organic solvents including thiophene.

Plumbination was observed by us in the following circumstances: when lead tetraisobutyrate was dissolved in excess thiophene, it was noted that, after the mixture had stood for several days at room temperature, a sample of the mixture did not give a typical reaction for the presence of a tetravalent lead salt on hydrolysis (formation of a light-yellow precipitate). Thus, the lead tetraisobutyrate had gradually disappeared.

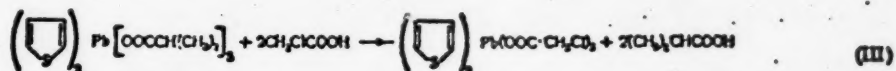
Under the conditions described in the experimental part, we were able to isolate and identify di- $\alpha$ -thienyllead diisobutyrate in the form of a white, crystalline material, the formation of which can presumably be described by the following successive reactions\*. The unstable thienyllead trisobutyrate is formed first by direct plumbination



which then undergoes disproportionation



Analysis, determination of the number of acid groups, and conversion to di- $\alpha$ -thienyllead di (monochloroacetate) according to

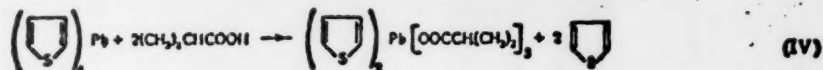


confirmed the formula of the compound.

\*Criegee and co-workers [6], in describing the preparation of compounds of the class  $ArPbX_2$  through the diaryllead compounds, failed to note that this method had been discovered and published by us almost a year earlier [7].

\*\*Another possible mechanism of the formation of  $(C_4H_5S)_2Pb[OOCCH(CH_3)_2]_2$  can be based on the metallating action of  $C_4H_5SPb[OOCCH(CH_3)_2]_4$  on thiophene.

In order to determine the place at which the lead entered the thiophene molecule, a known sample of di- $\alpha$ -thienyllead diisobutyrate was prepared from tetra- $\alpha$ -thienyllead [8] according to the reaction:



this sample was identical with the substance prepared by direct plumbination. Introduction in the "alpha" position, which is characteristic of thiophene in the case of other metal salts, is thus confirmed in the case of lead.

Thus, the direct introduction of metals lying in one row in the periodic table, Au, Hg, Tl and Pb, can now be considered completed by the plumbination reaction described here for the first time.

There is no doubt that this process is very slow as compared to the rapid mercuration and thalliation reactions.

### EXPERIMENTAL

Plumbination of thiophene. 6 g of lead tetraisobutyrate [8] (previously washed with petroleum ether) was dissolved (dissolved rapidly and smoothly) in 10 ml of thiophene (large excess based on Equation I) and allowed to stand at room temperature. After several days, the mixture gave only a slight test for the original tetraisobutyrate (light-yellow precipitate on dilution with water). After standing for 10 days, the mixture was diluted with 4 ml of absolute alcohol to decompose the unreacted lead tetraisobutyrate, and the mixture was then allowed to stand for two days.

The thiophene and alcohol were evaporated almost to dryness at room temperature. The semisolid precipitate was treated with 5 ml of benzene, the lead diisobutyrate was filtered, and the precipitate was diluted with 7.5 ml of hexane.

A white crystalline precipitate formed, m. p. 192° (with decomposition; darkening began at 186°).

Found %: Pb 37.70; 38.35

$(\text{C}_4\text{H}_3\text{S})_2\text{Pb}[\text{OOCCH}(\text{CH}_3)_2]_2$ . Calculated %: Pb 37.85.

The number of acid groups was 2.1. When added to concentrated sulfuric acid, the material decomposed with the formation of thiophene (addition of thiophene, then the usual test with isatin).

Di- $\alpha$ -thienyllead diisobutyrate is readily soluble in alcohol and acetone, moderately soluble in benzene in the cold and readily on heating, and sparingly in hexane.

The substance was identical with the diisobutyrate prepared from tetra- $\alpha$ -thienyllead (see below).

Di- $\alpha$ -thienyllead di (monochloroacetate). 0.55 g of di- $\alpha$ -thienyllead diisobutyrate, prepared in the preceding experiment, was dissolved at room temperature in 7 ml of benzene acidified with 7 drops of isobutyric acid. The solution was filtered from the suspension, and to the filtrate was added 0.4 g (double the theoretical (Equation III) amount) of a saturated solution of monochloroacetic acid in benzene. On the next day, the resulting white, finely crystalline precipitate was filtered and washed with benzene. The yield was 0.38 g (68%). The substance had an m. p. of 174° (with decomposition; gradual darkening began at 165°). An indophenine test for thiophene was positive.

Found %: Pb 37.40; 37.43; Cl 12.60; 13.00

$(\text{C}_4\text{H}_3\text{S})_2\text{Pb}(\text{OOCCH}_2\text{Cl})_2$ . Calculated %: Pb 37.00; Cl 12.66.

Di- $\alpha$ -thienyllead di (monochloroacetate) dissolves with difficulty in benzene, chloroform, dichloroethane, acetone, and alcohol even on heating, and is insoluble in petroleum ether, hexane, and ether.

Di- $\alpha$ -thienyllead diisobutyrate from tetra- $\alpha$ -thienyllead. 0.82 g of tetra- $\alpha$ -thienyllead, prepared from  $\alpha$ -thienylmagnesium bromide and lead tetrachloride [9], was heated with 1.5 ml of isobutyric acid to 60-70° on a water bath. After approximately half an hour, the precipitate dissolved. Heating was continued for another 15 minutes at this same temperature. A white, crystalline precipitate formed while the solution was still hot. The reaction mixture was diluted with 1.5 ml of petroleum ether to separate the product more completely, suction

filtered, and washed with petroleum ether. 0.55 g (67%) of a substance with an m. p. of 192° (with decomposition) was obtained.

Found %: Pb 38.05; 37.71.

The number of acid groups was 1.9. An Indophenline test for thiophene was positive.

The known di- $\alpha$ -thienyllead diisobutyrate prepared in this manner was identical with the above-described diisobutyrate prepared by the plumbination reaction.

The diisobutyrate was converted to di- $\alpha$ -thienyllead di (monochloroacetate); the latter was identical in properties with that described above.

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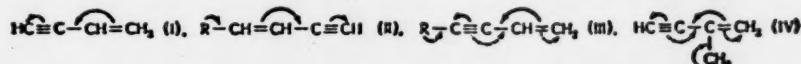
# THE DIPOLE MOMENTS AND REACTIVITY OF VINYLACETYLENIC HYDROCARBONS

A. A. Petrov, K. S. Mingaleva and B. S. Kupin

(Presented by Academician B. A. Arbuzov, July 4, 1958)

An investigation of addition reactions of 1,3-enyne hydrocarbons led to the conclusion that in molecules of vinylacetylene and *n*-alkenylacetylenes (II), the electron cloud is shifted in the direction of the triple bond [1]. In the case of vinylalkylacetylenes (III) and certain isoalkenylacetylenes (IV), the molecules must be considered to have a dual polarization which is reinforced in one direction or another, depending on the nature of the substituents; in the reaction with hydrogen halides, the order of addition indicated a shift of electrons in the direction of the triple bond [2], while in reactions with bromine, water, and alcohols, the shift was in the direction of the double bond [3, 4].

Such duality in the reactivity of vinylalkylacetylenes could be due to a weakening of the polarity of the enyne system owing to a partial shift of electrons, under the influence of the radicals, in a direction contrary to the usual shift in the 1,3-enyne system (III), (IV):



Some of the physical properties of the vinylalkylacetylenes also indicate such polarization.

By means of electron diffraction, it has been established that not only the  $\text{C}-\text{C}$  distance, but also the  $\text{CH}_3-\text{C}$  distance in the vinylmethylacetylene molecule is considerably shortened [5].

The intensity of the bands in the infrared spectra corresponding to double bonds was considerably higher in the case of hydrocarbons of types (III) and (IV) than in the case of hydrocarbons of type (II). It is possible to explain this by the great change in the polarity of the double bond during vibrations as a result of a shift of electrons toward it [6].

A final judgment as to the nature of the polarization in molecules of vinylacetylenic hydrocarbons can be formed only by determining their dipole moments.

There are data in the literature on the dipole moments of vinylacetylene, two of its phenyl derivatives [7], and also divinylacetylene and some other dienynic hydrocarbons [8].

From the data on the dipole moments of the phenylvinylacetylenes, it follows that a transfer of the phenyl group from the 1- to the 4-position of the 1,3-enyne system sharply changes the value of the dipole moment; 1-phenyl-1-buten-3-yne has a higher and 1-phenyl-3-buten-1-yne has a lower dipole moment than vinylacetylene. Consequently, the phenyl group causes a shift of the electron cloud in the same direction, in the first case, and in the opposite direction, in the second case, as in unsubstituted vinylacetylene.

Divinylacetylene is nonpolar. Vinylisopropenylacetylene has a somewhat lower dipole moment than vinylacetylene. Substitution at the end of the chain increases the moment.

We have measured the dipole moments of seven vinylalkylacetylenes containing the alkyl radicals  $\text{CH}_3-$ ,

TABLE 1

Expt. No.	Substance	Boiling point	$\epsilon$	$\mu$	MR	
					Found	Calc.
1	$\text{CH}_3\text{--CH--C}\equiv\text{C--CH}_3$	59--59.5°/760 mm	0.7402	1.4190	23.95	22.82
2	$\text{CH}_3\text{--CH--C}\equiv\text{C--CH}_2\text{--CH}_3$	83.5--84°/760 mm	0.7486	1.4519	28.87	27.44
3	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_2\text{--CH}_3$	108.5--109°/760 mm	0.7626	1.4550	33.50	32.06
4	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_3\text{--CH}_3$	62--62.5°/60 mm	0.7713	1.4560	38.13	36.68
5	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_4\text{--CH}_3$	59.5--60°/20 mm	0.7782	1.4580	42.85	41.29
6	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_5\text{--CH}_3$	76--76.5°/20 mm	0.7873	1.4598	47.37	45.91
7	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_6\text{--CH}_3$	110.5--111°/20 mm	0.7964	1.4620	56.71	55.16
8	$\text{CH}_3\text{--CH--C}\equiv\text{C--CH(CH}_3\text{) (cis)}$	44--44.5°/760 mm	0.7257	1.4340	23.72	22.82
9	$\text{CH}_3\text{--CH--CH--C}\equiv\text{CH (trans)}$	50--52°/760 mm	0.7270	1.4370	23.82	22.82
10	$\text{CH}_3\text{--C}\equiv\text{C--CH}$	32--32.5°/760 mm	0.7044	1.4151	23.50	22.82
11	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{--C}\equiv\text{C--CH} \\   \\ \text{C(CH}_3\text{)}_3 \end{array}$	97.5--98°/760 mm	0.7544	1.4330	37.27	36.68

TABLE 2

Expt. No.	Substance	$\epsilon$	$\nu$	$\mu$	$\delta$	P	$\mu$ , D
1	$\text{CH}_3\text{--CH--C}\equiv\text{C--CH}_3$	2,2832	1,1371	0.33	0.213	30.78	0.57
2	$\text{CH}_3\text{--CH--C}\equiv\text{C--CH}_2\text{--CH}_3$	2,2833	1,1371	0.40	0.190	36.95	0.62
3	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_2\text{--CH}_3$	2,2835	1,1370	0.31	0.174	42.43	0.65
4	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_3\text{--CH}_3$	2,2835	1,1370	0.21	0.159	46.27	0.63
5	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_4\text{--CH}_3$	2,2835	1,1370	0.19	0.150	51.48	0.65
6	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_5\text{--CH}_3$	2,2834	1,1370	0.20	0.132	56.91	0.67
7	$\text{CH}_3\text{--CH--C}\equiv\text{C--(CH}_2\text{)}_6\text{--CH}_3$	2,2835	1,1370	0.15	0.121	66.32	0.68
8	$\text{CH}_3\text{--CH--CH--C}\equiv\text{CH (cis)}$	2,2835	1,1372	0.93	0.240	38.73	0.85
9	$\text{CH}_3\text{--CH--CH--C}\equiv\text{CH (trans)}$	2,2835	1,1372	1.15	0.260	41.86	0.93
10	$\text{CH}_3\text{--C}\equiv\text{C--CH}$	2,2833	1,1373	0.136	0.282	29.78	0.55
11	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2\text{--C}\equiv\text{C--CH} \\   \\ \text{C(CH}_3\text{)}_3 \end{array}$	2,2835	1,1370	0.22	0.188	47.36	0.69

$\text{C}_2\text{H}_5\text{--}$ ,  $\text{C}_3\text{H}_7\text{--}$ ,  $\text{C}_4\text{H}_9\text{--}$ ,  $\text{C}_5\text{H}_{11}\text{--}$ ,  $\text{C}_6\text{H}_{13}\text{--}$ , and  $\text{C}_8\text{H}_{17}\text{--}$ , and also of cis- and trans-propenylacetylenes, isopropenylacetylene, and  $\beta$ -tert-butylvinylacetylene. The moment of phenylacetylene was also measured for comparison with the data of other authors. The following results were obtained:

1. The dipole moments of vinylmethyl- and isopropenylacetylene were considerably lower than the moment of vinylacetylene (0.77 D). Thus, the existence of a shift of electrons in a direction opposite to the shift in unsubstituted vinylacetylene has been proved experimentally.

2. With an increase in the size of the hydrocarbon radical, the dipole moment first increases somewhat and then remains approximately constant with a further increase in the size of the radical.

3. The dipole moments of cis- and trans-propenylacetylene are considerably higher than the moment of vinylacetylene, and the moment of the trans-form is higher than the moment of the cis-form in conformity with the three-dimensional models of these hydrocarbons.

Thus, it has been shown that in these compounds, there is a shift of electrons in the same direction as in unsubstituted vinylacetylene.

4.  $\beta$ -Tert-butylvinylacetylene has a higher moment than isopropenylacetylene. However, this moment is close to the moment of vinylbutylacetylene, and, therefore, these data cannot serve as direct proof of the presence of the Baker-Nathan effect in the isopropenylacetylene molecule.

Since the changes in the values of the dipole moment in all of the cases considered are due to the influence

of alkyl groups with a moment of the order of 0.35 D, and since the moment of vinylacetylene is twice this value, the assumption follows that in all of these cases, the moment is directed toward the triple bond.

Thus, the results of the measurements of the dipole moments of vinylacetylenic hydrocarbons confirmed the previously proposed concept, based on chemical data, of the mechanism of addition reactions at conjugated double and triple bonds.

#### EXPERIMENTAL

The vinylacetylenic hydrocarbons were prepared and purified by the usual methods [6]. The isoalkenyl-acetylenes were purified by distillation over phenylhydrazine and then were fractionated after being washed with 5% sulfuric acid. The cis- and trans-forms of isopropenylacetylene were separated by fractionation in a column [9].

The constants of the hydrocarbon samples used for the determinations are presented in Table 1.

The dipole moments were determined by the Debye method using dilute solutions [10]. The dielectric constants were determined by the beat method using a TKE-1 apparatus specially adapted for this purpose. After calibration of the liquid condenser, the error in the determination of  $\epsilon$  did not exceed 0.02%.

The measurements were carried out at 20° in benzene solutions with concentrations of the order of 1.0, 1.5, 2.0, 4.0, and 5.0%. The molecular polarization and the dipole moments were calculated by the usual formulas [10]. The atomic polarization was not taken into account. The results of the measurements and calculations are presented in Table 2. The dipole moment found for phenylacetylene (0.72 D) is in good agreement with the literature value [7].

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# PREPARATION AND PROPERTIES OF PHENAZINE SALTS (CONTRIBUTION TO THE QUESTION OF A CONNECTION BETWEEN CHEMICAL STRUCTURE AND THE ABILITY TO FORM FREE RADICALS AT THE NITROGEN)

Z. V. Pushkareva and L. B. Radina

(Presented by Academician N. I. Nazarov, November 20, 1956)

Free radicals in which the atom bearing the single electron is nitrogen include those of the diarylnitrogens [1] and the N-oxides of diarylnitrogens [2] and the hydrazyl [3] and certain other radicals [4]. Free radicals in the alloxazine [5] and phenazine [6] series belong to this same series of compounds. Free radicals of the latter group have not been well studied, but, in this connection, it is of great interest that a detailed study of their properties could lead to an explanation of the nature of certain biological oxidation-reduction processes. The preparation of a small number of derivatives of alloxazine and phenazine possessing properties of free radicals has been described in the literature. These are the so-called phenazyls, having the general formula (I) [6], and monoacetylphenazyl (II) [7] and the related radicals of flavone (III) [5], pyocyanine [8], and certain others.

We first turned our attention to the preparation of analogs of (II) containing acyl radicals differing in chemical nature in order to clarify the effect of the nature of the acyl group on the stability of radicals of this type. Since monoacetylphenazyl (II) was prepared by oxidation of monoacetyldihydrophenazine, for the preparation of its analogs a series of monoacyldihydrophenazines (V) - (XI) with different acyl groups was synthesized. Compounds (V) and (VI) have been described in the literature [9, 10], but compounds (VII) - (XI) were prepared by us for the first time. A brief characterization of their properties is presented in Table 1.

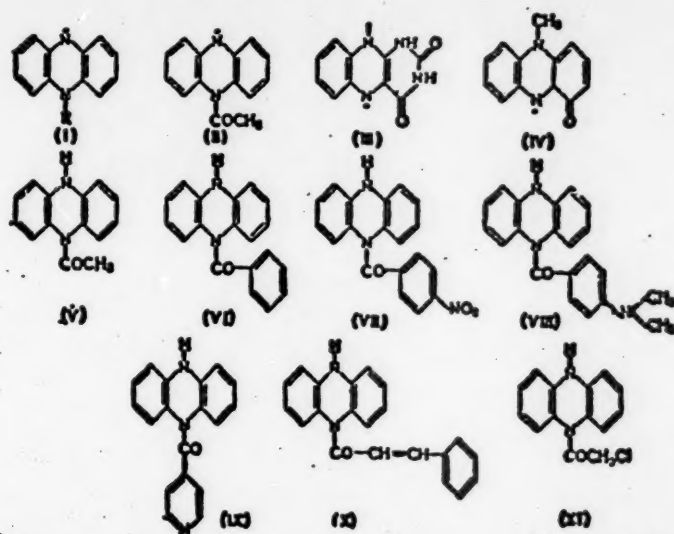


TABLE 1

Exp. No.	Compound obtained	Brief characterization of compound	$\mu_{\text{exp}} 10^{18}$	Maximum		Minimum	
				$\lambda_{\text{max}}$	lg $\epsilon$	$\lambda_{\text{min}}$	lg $\epsilon$
1	2	3	4	5	6	7	8
1	Monoacetyldihydrophenazine (V)	Fine, white crystals from alcohol, m.p. 254-255°		283	4,086	248	3,863
2	Monobenzoyldihydrophenazine (VI)	Slightly yellowish needles from alcohol, m.p. 224-226° Found %: N 9,65; 9,82 Calculated %: N 9,79	3,34	281	3,940	258	3,869
3	Mono-p-nitrobenzoyldihydrophenazine (VII)	Orange plates from alcohol, m.p. 211-213° Found %: N 12,90; 12,78 Calculated %: N 12,69	4,90	284	4,230	254	4,111
4	Mono-p-dimethylaminobenzoyldihydrophenazine (VIII)	White crystals from alcohol m.p. 230-231° Found %: N 12,52; 12,89 Calculated %: N 12,75		305	4,488	254	3,672
5	Mono-p-isonicotinoyldihydrophenazine (IX)	Pale yellow needles from alcohol, m.p. 271-272° Found %: N 14,74 14,59 Calculated %: N 14,63	6,18	272	4,119	248	3,929
6	Mono-p-cinnamoyldihydrophenazine (X)	Bright yellow crystals from alcohol, m.p. 223-224° Found %: N 8,77; 8,90 Calculated %: N 8,97	2,88	283	4,505	251	4,068
7	Mono- $\alpha$ -chloroacetyldihydrophenazine (XI)	White, finely crystalline precipitate from alcohol, m.p. 231-232° Found %: N 11,09; 10,98 Calculated %: N 10,80		278	3,823	254	3,672
8	Diphenylamine			284	4,440	248	3,580
9	Product of the oxidation of monoacetyldihydrophenazine with anhydrous ferric chloride (XII)	Greenish orange crystals, m.p. 195-197° Found %: N 9,70; 9,28; Cl 29,79; 28,98 Calculated %: N 9,45; Cl 29,71	-	-	-	-	-
10	"Orange" product (XIII)	Golden orange crystals from isoamyl alcohol, m.p. 191-193° Found %: N 10,32; 10,48 Cl 20,78; 20,76 Fe 10,66; 10,38 Calculated %: N 10,71 Cl 20,38; Fe 10,71		248 362	4,860 4,530	287	3,498
11	Phenazine hydrochloride (XIV)	Greenish yellow crystals from isoamyl alcohol, m.p. 195-197° Found %: N 12,31; 12,52 Calculated %: N 12,93		248 360	4,780 4,180	280	1,000



Fig. 1

Measurement of the dipole moments of the individual substances (in benzene at 25°, see Table 1) and calculation of the dipole moments for various configurations of these compounds by vector summation showed that in all of these cases the experimental dipole moment is close to the value calculated for a nonplanar configuration of the dihydrophenazine part of the molecule. Moreover, in these compounds the acyl group is, as a rule, trans with respect to the phenolic ring in the dihydrophenazine part of the molecule and is cis with respect to the hydrogen of the NH group as is shown in Figure 1, which is a photograph of a ball model of a molecule of monobenzoyldihydrophenazine. From this, it can be assumed that the acyl group, which with such configuration is isolated from conjugation with the benzene rings, cannot exert any substantial influence on the properties of the NH bond in monoacyldihydrophenazines. The results obtained in determining the absorption spectra of the monoacyldihydrophenazines in the u. v. region (Table 1) are experimental confirmation of this assumption.

As seen from the data of Table 1, the spectra of the monoacyldihydrophenazines are very similar to each other and to the spectrum of diphenylamine, in which there is no acyl group.

Oxidation in the monoacyldihydrophenazine series has been previously studied on only one example, the oxidation of monoacetyldihydrophenazine with anhydrous ferric chloride in chloroform solution [7]. Two products were obtained from this reaction: violet-black crystals with a m. p. of 137°, for which was proposed the structure of a molecular compound of monoacetyldihydrophenazine (V) with a molecule of monoacetylphenazine (II), and an "orange" substance with a m. p. of 191-193°, which was considered to be a dimer of monoacetylphenazine (II). Carrying out the oxidation of three different monoacyldihydrophenazines, (V), (VI), and (VII), under analogous conditions with an excess of ferric chloride unexpectedly led to the formation of the same oxidation product with an m. p. of 195-197°, which was converted, in turn, to a substance identical with the previously known "orange" product with a m. p. of 191-193°.

A detailed study of the chemical structure and properties of the monoacetyldihydrophenazine oxidation product melting at 191-193° showed that the substance does not contain acetyl groups and, consequently, is the product of the oxidative deacylation of monoacetyldihydrophenazine; it is a complex involving trivalent iron; it has a chlorine content of 20.78% and a nitrogen content of 10.48%. Moreover, the compound is strongly paramagnetic ( $\chi_g = 24 \cdot 10^{-6}$  m. u.). The ultraviolet spectrum of the "orange" substance is similar to the spectrum of phenazine and completely unlike the spectrum of monoacetyldihydrophenazine, as may be seen from the graph (Figure 2).

In addition, it was observed that the substance obtained during oxidation of monoacetyldihydrophenazine initially possessed properties of a free radical, forming dark-green solutions when heated in isoamyl alcohol, for example, but during purification by repeated recrystallization from isoamyl alcohol the compound completely

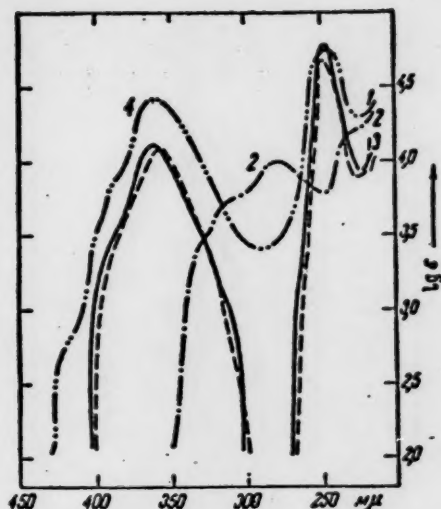
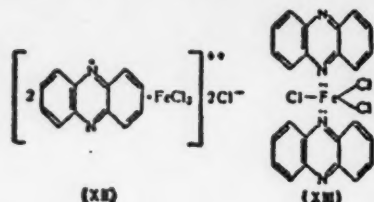


Fig. 2. Absorption spectra of: 1) phenazine, 2) monoacetyldihydrophenazine, 3) phenazinium chloride, 4) "orange" product with an m. p. of 191-193°

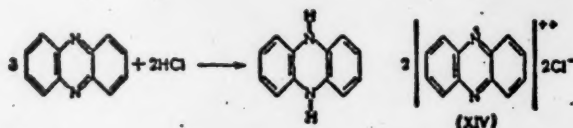
lost this property, and the "orange" substance with a m. p. of 191-193° was completely incapable of dissociating with the production of a green color. The "orange" substance, as well as the initially obtained product with the properties of a free radical, was very easily hydrolyzed by water, being converted to phenazine.

On the basis of these data, formula (XII) is proposed for the monoacetyldihydrophenazine oxidation product which possesses the properties of a free radical; this formula includes two molecules of phenazinium chloride of Weitz amine-salt type) coordinated with a molecule of  $\text{FeCl}_3$ . The "orange" product with a m. p. of 191-193° is evidently a product of a series of transformations of the phenazinium cation, and it contains two molecules of phenazine bound in a complex with a molecule of  $\text{FeCl}_3$  (XIII).

The structure of the latter was confirmed by synthesis from phenazine and ferric chloride.

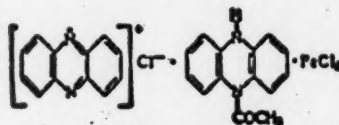


An attempt was also made to confirm experimentally the formation of the phenazinium cation by preparing it in the free state rather than in the form of a complex. Actually, it was found that phenazine, on reaction in an anhydrous medium with hydrogen chloride, forms a greenish-yellow, crystalline substance with a m. p. of 195-197° and which was soluble in isoamyl alcohol with the formation of a dark-green color. The reaction apparently proceeds according to the scheme:



The structure of the substance with a m. p. of 195-197° (XIV) was confirmed by analysis and by determination of the magnetic susceptibility. Substance (XIV) was paramagnetic ( $\kappa_g = 6,5 \cdot 10^{-6}$  m. u.), which corresponds to the presence of one unpaired electron in the molecule. It was converted to phenazine by repeated heating of the solutions and also by the action of water (just as (XII) was converted to the "orange" substance (XIII)). The absorption spectrum of this compound (Figure 2, Spectrum 3) was identical to the spectrum of phenazine, which also confirms the structure assigned to it as that represented by formula (XIV).

On the basis of the analytical results and of a study of the chemical properties of the intermediate "black" monoacetyldihydrophenazine oxidation product, m. p. 137°, it was shown that this compound is a complex of one molecule of  $\text{FeCl}_3$  and a molecular compound of phenazinium chloride (XIV) with a molecule of monoacetyldihydrophenazine (V).



As a result of our work, it has been shown that phenazine can form free radicals which are not analogs of the diarylnitrogen free radicals (as has been assumed up to the present in all cases I-IV), but which are related to the amine salt type (phenazinium salts). Phenazinium chloride is paramagnetic in crystals, gives deeply colored solutions in anhydrous, but polar, organic solvents, displays a tendency toward the formation of complexes, and is instantaneously hydrolyzed by water.

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## SYNTHESIS OF RUTIN

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(Presented by Academician A. N. Nesmelanov, June 30, 1958)

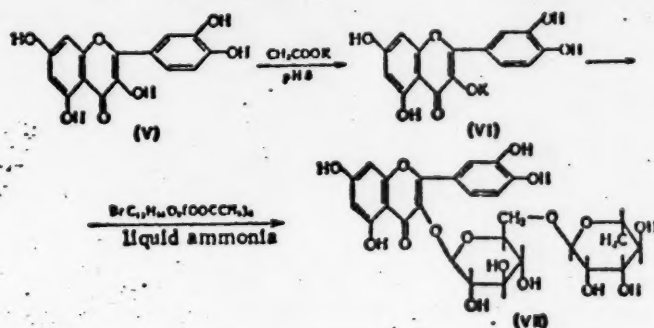
Rutin, quercetin-3-rutinoside (VII), the active principle of vitamin P, hesperidin, eriodictin, and certain other catechins are very valuable, since they have the ability (especially in combination with ascorbic acid) to decrease the permeability and brittleness of the capillaries.

The presence of five hydroxyl groups in the quercetin molecule makes it very difficult to prepare its 3-glycosides (V). Moreover, the reactivity of the hydroxyl group in the 3-position of quercetin is lowered by hydrogen bonding with the oxygen of the pyran carbonyl group [1, 2].

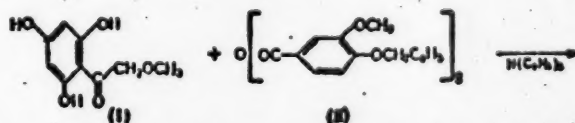
The formation of a glycoside bond at the 3-position by the Koenigs - Knorr method, by the action of acetobromoglucose in quinoline in the presence of active silver oxide, is successful only for the simplest flavonoles and is accompanied by replacement of the free phenolic groups [3, 4].

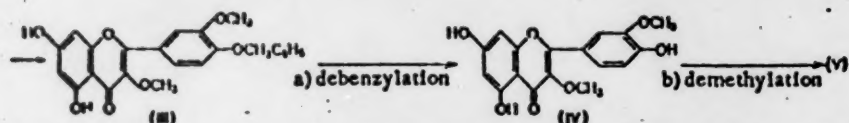
In 1952, Ice and Wender [5] successfully carried out the preparation of isoquercitrin, 3-glucosidoquercetin [3, 3', 4', 5, 7-pentahydroxyflavone-3-glucoside], by the action of  $\alpha$ -acetobromoglucose on the 3-potassium salt of quercetin in solution in liquid ammonia. The synthesis of rutin itself or of other 3-disaccharides is still unknown.

In the present paper, we describe the preparation of rutin from quercetin and  $\alpha$ -acetobromorutinoside according to:



The initial quercetin was prepared by the method of Allan and Robinson [6] with the exception that protection of the hydroxyl group in the vanillic acid was accomplished by benzylation; triethylamine was used as the condensing agent [7].





The disaccharide of  $\alpha$ -aceto- $\beta$ -1-L-phamnosido-6-D-glucose,  $\alpha$ -acetobromorutnose, was synthesized by the method of Zemplen [8] from aceto- $\beta$ -hamnose and acetochloroglucose.

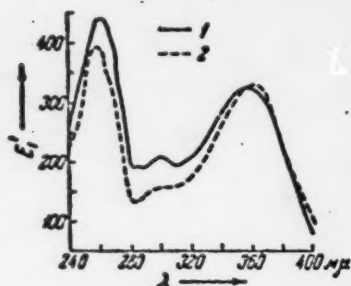


Fig. 1. U. v. absorption spectra of rutin (in 96% alcohol): 1) synthetic, 2) natural.

Tests by paper chromatography and a comparison of the u. v. absorption spectra (Figure 1) showed that the synthetic and natural rutins were identical.

In addition, the action of liquid ammonia on quercetin was accompanied by partial decomposition of the latter, and in this connection, paper chromatography of the synthetic rutin disclosed the presence of an impurity with a u. v. absorption maximum characteristic of the decomposition products of quercetin.

Our preparation of rutin constitutes the completion of its total synthesis.

## EXPERIMENTAL

### A. 5,7,4'-trihydroxy-3,3'-dimethoxyflavone (IV).

2.5 g (0.0126 mole) of  $\omega$ -methoxyphloroacetophenone (I) and 31.5 g (0.063 mole) of the anhydride of  $o$ -benzylvanillic acid (II) were powdered, mixed with 7.65 g of

triethylamine, and heated for 4 hours at 150-160°. The cooled melt was dissolved in 200 ml of alcohol and 35 ml of water containing 25 g of potassium hydroxide, the resulting solution was refluxed 30 minutes, and the alcohol was evaporated under reduced pressure. The residue was dissolved in 200 ml of water and saturated with carbon dioxide. A yellow-green precipitate (3.41 g) of 5,7-dihydroxy-4'-benzyloxy-3,3'-dimethoxyflavone (III) was formed. The entire precipitate was heated for an hour on a boiling water bath with 135 ml of glacial acetic acid and 63 ml of concentrated hydrochloric acid. The solution was decanted into water and allowed to stand overnight. 5,7,4'-Trihydroxy-3,3'-dimethoxyflavone (IV) separated in the form of fine crystals. After three-fold recrystallization from alcohol, the yield was 1.32 g (31.6% based on the  $\omega$ -methoxyphloroacetophenone). M. p. 258-259°.

Found %: C 61.72; H 4.56

$C_{17}H_{14}O_7$ . Calculated %: C 61.82; H 4.27

B. 3,5,7,3',4'-pentahydroxyflavone (quercetin) (V). 420 mg of 5,7,4'-trihydroxy-3,3'-dimethoxyflavone (IV) and 18 ml of freshly distilled hydriodic acid (b. p. 125-126°) were heated on an oil bath for 2 hours to 150-155°. The fine, bright yellow crystals were filtered and recrystallized from 70% alcohol. The yield was 300 mg (78.1%). M. p. 311-312°. A mixed sample with natural quercetin showed no melting point depression,  $\lambda_{max}$  375 and 255 m $\mu$   $E_{1cm}^{1\%}$  719 and 671, respectively.  $R_f$  0.38, in 60% acetic acid.

Found %: C 59.48; H 3.56

$C_{15}H_{10}O_7$ . Calculated %: C 59.61; H 3.34

C. Quercetin-3-rutinoside (rutin) (VII). a. The potassium salt of quercetin (VI). 0.7 g (0.00232 mole) of quercetin (V) was dissolved in 50 ml of alcohol, and 14 ml of alcohol containing 0.84 g (0.00857 mole) of potassium acetate was added. During the precipitation, the pH of the solution was maintained at about 8 by the addition of alcoholic potassium hydroxide. The precipitated potassium salt of quercetin was filtered and washed with alcohol. The yield was 0.74 g.

b. Quercetin-3-rutinoside (VII). To 75 ml of distilled liquid ammonia were added 0.3 g (0.00088 mole) of the K salt of quercetin (VI) and 0.85 g (0.00132 mole) of  $\alpha$ -acetobromorutnose ( $\alpha$ -acetobromo- $\beta$ -1-L-phamnosido-6-D-glucose). The ammonia was evaporated, 75 ml of dry methyl alcohol was added to the residue, and the mixture was allowed to stand for 24 hours. The mineral precipitate was filtered, the methyl alcohol was distilled from



Fig. 2. Paper chromatograms of synthetic and natural rutin and of their mixture in 15% acetic acid: 1) synthetic rutin ( $R_f$  0.60), 2) mixture of synthetic and natural rutin ( $R_f$  0.59), 3) natural rutin ( $R_f$  0.60)

spot fluorescing with  $R_f$  of 0.145 (Figure 2, 1a and 2a) and a yellow spot with  $R_f$  of 0.77 (1b and 2b).

The spot with an  $R_f$  of 0.145 contained the original sugar, and the spot with an  $R_f$  of 0.77 contained a substance having an intense u. v. absorption with a maximum in the region of 290-295 m $\mu$ .

All-Union Vitamin Scientific Research Institute

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the filtrate under reduced pressure, and 0.83 g of raw synthetic rutin was obtained. For purification, a 60-mg sample of the substance was dissolved in 20 ml of ethyl alcohol and subjected to paper chromatography (120-density filter paper produced by the Volodarsk factory). Distribution was by 23% isopropyl alcohol, and the spot was determined with a fluoroscope ( $R_f$  0.53). The substance was eluted with ethyl alcohol.

For comparison of the natural and synthetic rutins, spots of alcoholic solutions of the rutins were placed on the paper as follows: 1) synthetic, 2) a mixture of synthetic and natural, and 3) natural. Distribution was by 15% acetic acid, and the developer was a 1% alcoholic solution of aluminum chloride. The fluoroscope showed spots of an intense yellow, the  $R_f$  of which was 0.60 for the natural and synthetic samples and 0.59 for their mixture.

For the synthetic rutin and its mixture with the natural product, two other spots were observed on the chromatogram by means of the fluoroscope: a green

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# COMPLEX COMPOUNDS OF TRIVALENT COBALT WHICH CONTAIN THIOUREA

A. V. Ablov and N. M. Samus\*

(Presented by Academician I. L. Cherniaev, June 26, 1958)

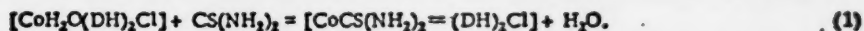
Thiourea (thio) gives products by combination with salts of polyvalent metals [1-3].

In the chemistry of divalent platinum, the well-known reaction of N. S. Kurnakov which uses this reagent permits a clear-cut solution of the question of whether a compound with the composition  $(PtA_2X_2)$  has a cis or trans structure [4].

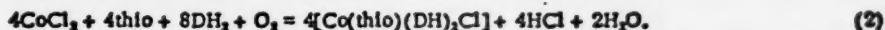
Only a few comparatively unstable compounds of thiourea with salts of divalent cobalt are known [5]. Compounds of trivalent cobalt which contain this addend in the inner coordination sphere have not been previously described.

In continuation of the study of complex compounds of trivalent cobalt with dimethylglyoxime, we have succeeded in introducing thiourea into the inner coordination sphere. A study of the reactions of this compound shows that thiourea has an increased trans effect in glyoximes of trivalent cobalt.

In the reaction of chloro-bis-dimethylglyoxime aquocobalt with water or alcohol solutions of thiourea in the ratio 1:1, even at room temperature there is formed a good yield of yellow-brown, finely crystalline substance which is chloro-bis-dimethylglyoxime thiocarbamide cobalt. The reaction occurs by the following equation:



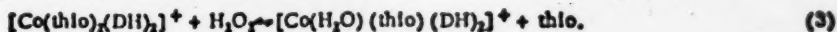
This substance can be obtained in the usual way, described by L. A. Chugaev [6], namely: by air oxidation of an alcoholic solution of cobalt chloride (1 mole), dimethylglyoxime (2 moles) and thiourea (1 mole). The reaction can be summarized by the equation:



When it is gently heated with a water or alcohol solution of thiourea, chloro-bis-dimethylglyoxime thiocarbamide cobalt dissolves and then from the solution crystals of bis-dimethylglyoxime dithiocarbamide cobalt chloride precipitate  $[Co(thio)_2(DH)_2Cl] \cdot 5H_2O$ .

The latter compound can be obtained by oxidation in air of an alcoholic solution of cobalt chloride (1 mole), dimethylglyoxime (2 moles), and thiourea (more than 2 moles). In this way we obtained other salts with the composition  $[Co(thio)_2(DH)_2]X$  where  $X = BrNO_3$ . When these salts are placed in water they easily lose one molecule of thiourea and change into the difficultly soluble compounds with the composition  $[Co(thio)(DH)_2]X$ . This reaction is reversible and the compounds which precipitate can easily be redissolved in water by adding thiourea. By the use of these properties, double decompositions can be carried out with salts of the complex cation  $[Co(thio)(DH)_2]^+$ . Also, when salts of the alkali metals  $MeX$  are added to solutions which contain the cation  $[Co(thio)(DH)_2]^+$ , the nonelectrolytes with the composition  $[Co(thio)(DH)_2]X$  precipitate in the pure state.

We will consider the different bonds for the two molecules of thiourea in the complex  $[Co(thio)_2(DH)_2]^+$ . One thiourea molecule is split and recombined very easily; it is very mobile. Certainly this reaction goes through formation of an aquo cation  $[Co(H_2O)thio(DH)_2]^+$  by the equation



The second molecule of thiourea is not removed in a neutral medium by the action of a large excess of the salt  $MeX$  (where  $X = Cl, Br, NO_3, I, CNS$ ) or by raising the temperature.

As one of us has shown, on the basis of the trans effect rule of I. I. Cherniaev [7], in dioximes of trivalent cobalt, two dimethylglyoxime residues lie in one plane [8]. Hence, in the complex cation  $[Co(thio)_2(DH)_2]^+$  two molecules of thiourea are in the trans position to each other. This fact has a natural explanation if we assume that thiourea in dioxime cobalts has a higher trans effect in reactions which proceed in a neutral medium than do the acid residues  $Cl, Br, NO_3, I$ , and  $CNS$ .

## EXPERIMENTAL PART

1. Chloro-bis-dimethylglyoxime thiocarbamide cobalt  $[Co(thio)(DH)_2Cl]^+$ . I. To 3.4 g of chloro-bis-dimethylglyoxime aquocobalt  $[CoH_2O(DH)_2Cl]$  [9] and 0.76 g of thiourea was added - 100 ml of water. When the mixture was stirred, even at room temperature, but better with gentle heat, the brownish green aquo compound changed to a yellow finely crystalline substance which was filtered and washed with water, alcohol, and ether. Yield 80% of the theory. The compound was very difficultly soluble in water, somewhat better soluble in alcohol and ether. A solution of silver nitrate in the cold did not precipitate silver chloride; with heating, cloudiness appeared. Under the microscope the crystals had the form of yellow prisms. The air-dried substance was used for analysis.

Found%: Co 14.52; 14.43; S 7.90  
 $[Co(CH_3)_2S(C_4H_7N_2)_2Cl]$ . Calculated %: Co 14.71; S 8.00

II. 11.7 g of dimethylglyoxime were dissolved with heat in 150 ml of alcohol. The solution was filtered hot and to it was added 12.0 g of cobalt chloride, 3.8 g of thiourea, and a strong stream of air was passed in for 3 hours. Yield 90% of the theory.

Found %: Co 14.41; Cl 8.87; 8.44; 8.60; S 8.28; 8.43; N 21.23; 20.91  $[Co(CH_3)_2S(C_4H_7N_2O_2)_2Cl]$ .  
 Calculated %: Co 14.71; Cl 8.85; S 8.00; N 20.98

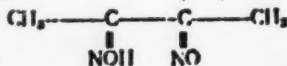
2. Bis-dimethylglyoxime dithiocarbamide cobalt chloride  $[Co(thio)_2(DH)_2]Cl \cdot 5H_2O$ . I. 4.0 g of chloro-bis-dimethylglyoxime thiocarbamide cobalt (1 mole) and 2.3 g (3 moles) of thiourea were heated on a water bath with 50 ml of water. The difficultly soluble chloromonothiocarbamide compound easily formed a dark brown solution from which a red brown precipitate of long tetragonal prisms settled out on cooling. The substance was filtered, washed two or three times with water, and then with an alcohol solution of thiourea. A new portion of the substance separated from the mother liquors when they were evaporated in air. They dissolved easily in a water solution of thiourea. The water of crystallization was lost very easily, in part when they were kept in air and completely in a desiccator over phosphoric anhydride.

II. Heating chloro-bis-dimethylglyoxime aquocobalt with a water solution of thiourea, using 3-4 moles, converted this substance first into the monothiocarbamide compound which then went into solution and well formed long prisms gradually separated. Excess thiourea did not change the reaction. The substance could be recrystallized from water which contained some thiourea.

III. The substance could be obtained best and with a very good yield (up to 80% of the theory) in the following way: a hot solution of 12.0 g of cobalt chloride in 30 ml of ethyl alcohol was mixed with 11.7 g of dimethylglyoxime in 150 ml of alcohol. To the filtered mixture was added 8-9 g, that is, somewhat more than 2 moles of thiourea and air was passed in for 4 hours. Crystals of the dithiocarbamide complex gradually precipitated. To obtain larger crystals we heated the mixture on the water bath and cooled it slowly. Freshly prepared substance dried between sheets of filter paper was used for analysis.

Found %: I. Co 10.29; S 11.40  
 II. Co 10.40; S 11.25  
 III. Co 10.44; 10.30; Cl 6.38; S 11.65; N 19.66; loss over  $P_2O_5$  16.16  
 $[Co(CH_3)_2S(C_4H_7N_2O_2)_2]Cl \cdot 5H_2O$ . Calc. %: Co 10.39; Cl 6.25; S 11.30; N 19.76;  $H_2O$  15.87

\* DH means the dimethylglyoxime residue



3. Bis-dimethylglyoxime dithiocarbamide cobalt bromide  $[\text{Co}(\text{thio})(\text{DH})_2]\text{Br} \cdot 2\text{H}_2\text{O}$ . The substance was obtained in the form of dark-brown prisms by method III described for the preceding compound, with yields of 75% of the theory. The substance did not lose water of crystallization over phosphoric anhydride. The water could be removed only by heating to 105°.

Found %: Co 10,47; 10,45; S 11,01; loss in weight at 105° 6,54  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2]\text{Br} \cdot 2\text{H}_2\text{O}$ . Calculated %: Co 10,57; S 10,96;  $\text{H}_2\text{O}$  6,46

4. Bis-dimethylglyoxime dithiocarbamide cobalt nitrate  $[\text{Co}(\text{thio})(\text{DH})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ . This was obtained like the preceding compound. Yield 70% of the theory.

Found %: Co 10,71; 10,74; 10,81; S 14,51  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ . Calculated %: Co 10,93; S 14,93

5. Bis-dimethylglyoxime dithiocarbamide cobalt iodide  $[\text{Co}(\text{thio})(\text{DH})_2]\text{I} \cdot 2\text{H}_2\text{O}$ . This compound was obtained by double decomposition in the presence of excess thiourea.

3.0 g of bisdimethylglyoxime dithiocarbamide cobalt nitrate and 1.0 g of thiourea were dissolved with gentle heat in about 75 ml of water. 1 g of potassium iodide was added to the still hot solution. Long prisms gradually separated; they were filtered and washed with water, then with an alcohol solution of thiourea.

Found %: Co 9,64; 9,82; S 5,50  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2]\text{I} \cdot \text{H}_2\text{O}$ . Calculated %: Co 9,76; S 5,29

6. Bromo-bis-dimethylglyoxime thlocarbamide cobalt  $[\text{Co}(\text{thio})(\text{DH})_2]\text{Br}$ . 3.0 g of bis-dimethylglyoxime thlocarbamide cobalt nitrate and 1-2 g of potassium bromide were treated with water. The nitrate was gradually converted to a difficultly soluble dark-brown substance which was filtered and washed many times with water, alcohol, and ether. Under the microscope the substance had the form of long, dark-yellow prisms.

Found %: Co 13,14; Br 18,08; S 7,58  
 $\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Br}$ . Calculated %: Co 13,24; Br 17,96; S 7,20

In an analogous way we obtained other compounds of the type  $[\text{Co}(\text{thio})(\text{DH})_2\text{X}]$ .

7. Nitro-bis-dimethylglyoxime carbamide cobalt  $[\text{Co}(\text{thio})(\text{DH})_2\text{NO}_2]$ . A brick-yellow, finely crystalline precipitate, difficultly soluble in water and organic solvents.

Found %: Co 14,29; 14,00; 14,08; S 8,13  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{N}_2\text{O}_2]$ . Calculated %: Co 14,33. S 7,79

8. Isothiocyanato-bis-dimethylglyoxime thlocarbamide cobalt  $[\text{Co}(\text{thio})(\text{DH})_2\text{NCS}]$ . Difficultly soluble in water, better in organic solvents. Under the microscope it has the form of light-brown prisms.

Found %: Co 13,60; 13,74; S 15,73  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{NCS}]$ . Calculated %: Co 13,92; S 15,14

9. Iodo-bis-dimethylglyoxime thlocarbamide cobalt.  $[\text{Co}(\text{thio})(\text{DH})_2\text{I}]$ . A dark-brown, finely crystalline substance. Almost insoluble in water. The action of excess potassium iodide on this substance does not cause any change, even with heating.

Found %: Co 12,21; 11,98; I 25,93; 26,05; S 6,74  
 $[\text{Co}(\text{CH}_3\text{N}_2\text{S})(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{I}]$ . Calculated %: Co 11,97; I 25,78; S 6,52.

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## THE NATURE OF THE BOND BETWEEN THE CENTRAL ATOMS AND SOME UNSATURATED MOLECULES IN COMPLEX PLATINUM COMPOUNDS

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(Presented by Academician V. I. Spitsyn, July 7, 1958)

The question of the bond between the metal and unsaturated molecules in complex platinum compounds is of great interest in connection with the general investigation of the nature of chemical bonds. Numerous workers who have studied this subject have been cited in the reviews of Keller and Chatt [1]. A. D. Gel'man [2] offered a theory according to which the platinum atom in the formation of complex compounds with unsaturated molecules acted simultaneously as an electron donor and acceptor. Therefore there was formed a double covalent bond between the central atom and the olefin. Ia. K. Syrkin [3] assumed that the unsaturated hydrocarbons  $C_2H_4$ ,  $C_3H_4$ , and others, were bound to a considerable extent covalently to platinum. Chatt and Duncanson [4] suggested a scheme for the formation of bonds between olefin molecules and platinum in complex compounds which could be characterized as a  $\pi$ -electron reaction. The basis of this scheme was found in the infrared absorption spectra of a series of complex compounds of platinum with olefins. However, the interpretation of the observed spectra given by Chatt and Duncanson seems unconvincing to us.

Chatt and Duncanson found a very weak absorption band in the spectrum above  $3000\text{ cm}^{-1}$ . In individual olefin hydrocarbons this band depends on the valence oscillation of CH in the group  $=CH_2$  and is very intense. One of the characteristic frequencies of the olefin molecule is the frequency of valence oscillation of the double bond  $C=C$  with a wave number about  $1650\text{ cm}^{-1}$ . In complex compounds of platinum with olefins this frequency is not found. In the infrared spectra of complexes of platinum with propylene and the dimeric complexes of platinum with ethylene and propylene, the authors mentioned found absorption bands whose maxima corresponded to wave number  $1504\text{--}1506\text{ cm}^{-1}$ . Chatt and Duncanson ascribed these absorption bands to the oscillation frequency of the double bond  $C=C$ , displaced from the frequency in the corresponding isolated molecule of addend. This assumed displacement of frequency (by about  $130\text{ cm}^{-1}$ ) is explained by these authors from the formation of a bond between the olefin and platinum. On the basis of these interpretations of the two spectral characteristics, Chatt and Duncanson came to the conclusion that the double bond of the olefin is retained in the formation of the complex. This conclusion, without a test, has also been accepted in the work of Jonassen and Field [5]. We feel, however, that there is not sufficient basis for this.

The authors of the present communication have set up the problem of making a critical analysis of the infrared spectrum of the complex compounds of platinum with ethylene, propylene, and carbon monoxide. We have reproduced the infrared spectra of the first two compounds and studied the spectra of the cis and trans forms of  $K[PtCl_2(C_2H_4)_2]$ . We have calculated the skeletal oscillations of the system  $(CH_2)_2Pt$  and studied the secular equation of the trans-form  $[PtCl_2(C_2H_4)_2]^-$ .

The number and values for the frequencies of the infrared absorption bands of platinum with ethylene and propylene basically corresponded to the work of [4-6].

We consider the general spectral characteristics of the complex compounds of platinum with olefins.

1. In contrast to Chatt and Duncanson [4], the presence of frequencies above  $3000\text{ cm}^{-1}$  in the infrared spectra of these complexes is accepted as a necessary, but still not sufficient sign of the retention of the double bond  $C=C$  in the olefin part of the complex. The absorption bands in this part of the spectrum occur also in such molecules as ethylene oxide, ethylene sulfide, ethylene imine, and cyclopropane. As theoretical work and



calculations have shown [7], this depends on the close similarity of the electronic configuration in the  $\text{CH}_2$  group of the molecules of ethylene, ethylene oxide, and cyclopropane. This similarity permits us to express the opinion that the olefin forms with platinum compounds of the type of a triangular cyclic structure.

2. By analogy with the preceding, the frequencies of the ethylene and propylene complexes with platinum found in the field  $1490\text{--}1510\text{ cm}^{-1}$  more truly belong to a deformed oscillation of  $\text{CH}_2$  (as has been established by strict calculation for cyclopropane and deuterocyclopropane [7a] and also as an interpretation for the oscillation spectrum of ethylene oxide) and not a frequency of oscillation of the double bond  $\text{C}=\text{C}$ .

3. The frequency of nonplanar deformative oscillation of the  $\text{CH}$  group is characteristic for olefins [8]. In the ethylene molecule it is  $949\text{ cm}^{-1}$  and is very intense in the infrared spectrum. The absence of this frequency in the spectrum of  $\text{K}[\text{PtCl}_2\text{H}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  and the presence of four supplementary intense oscillation frequencies in the field from  $1300$  to  $700\text{ cm}^{-1}$  as compared to the spectrum of the starting addend indicates considerable rebuilding of the ethylene molecule. This can be connected only with the rearrangement of the double bond  $\text{C}=\text{C}$  into a single one.

4. Such ideas are found in respect to the data on the structure of  $\text{K}[\text{PtCl}_2\text{H}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  obtained by G. B. Bokil and G. A. Kukina [9], according to which the ethylene molecule is arranged perpendicular to the plane of  $\text{PtCl}_2$  and is almost symmetrically related to it. The distance between the carbon atoms is  $1.50\text{ \AA}$ , that is, a value characteristic for a single bond between these atoms. Utilization of the structural parameters of this compound permits calculation of the frequencies and force constants of the triangular model of the  $(\text{CH}_2)_2\text{Pt}$  complex. For the sake of simplicity we have not considered the effect of oscillation of the chlorine atoms since it is known that reactions transmitted through heavy atoms are usually small. The  $\text{CH}_2$  group is taken as one atom. It is also assumed that in the case considered the model of the central energy was true. Calculation showed that the frequencies central energy was true. Calculation showed that the frequencies  $1188$ ,  $500$ , and  $632\text{ cm}^{-1}$  belonged to "ring" oscillations and the force constants between the carbon atoms were  $\text{C-C} = 4.7 \cdot 10^5\text{ dyne/cm}$ ; between the platinum and carbon atoms  $\text{Pt-C} = 3.2 \cdot 10^5\text{ dyne/cm}$ .

5. Analysis of the infrared spectrum of the complex compound  $\text{K}[\text{PtCl}_2\text{H}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  shows that the double bond  $\text{C}=\text{C}$  in the ethylene is changed into a single bond when it enters the inner sphere of the platinum atom and the strength of the bond between the platinum and the carbon atom is of the order of magnitude of the strength of an ordinary covalent bond.

6. The ideas expressed in points 1-3 relate equally to the complex compound  $\text{K}[\text{PtCl}_2\text{H}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ . On this basis the authors consider that its structure and the nature of the bonds formed by propylene with the central atom are analogous to the structure and nature of the bonds of ethylene with platinum in its complex compounds.

7. The infrared spectra of the complex cis and trans forms of  $\text{K}[\text{PtCONH}_2\text{Cl}_2] \cdot \text{H}_2\text{O}$  were studied. For the trans form we set up the secular equation, a study of which showed that in the matrix of the force coefficient the group of atoms  $\text{O-C-Pt}$  could be considered an isolated triangular molecule. The observed spectrum could be considered an isolated triangular molecule. The observed spectrum could be explained by accepting the assumption of a linear combination of a molecule of ethylene oxide with platinum. The force constant of the bond  $\text{Pt-C}$  is  $3.38 \cdot 10^5\text{ dyne/cm}$  and the force constant of deformative oscillation connected with change in angle  $\text{O-C-Pt}$  is  $0.5 \cdot 10^5\text{ dyne/cm}$ .

The calculated force constants for complex compounds of platinum with ethylene and with carbon monoxide agree with the literature data [10].

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### THREE TYPES OF KINETIC CURVES FOR THE REACTION OF METHANE AND PROPANE WITH NITROGEN DIOXIDE

A. P. Ballod, S. I. Molchanova, Academician A. V. Topchiev,  
T. V. Fedorova, and V. Ia. Shtern

The kinetics of the vapor-phase nitration of methane and propane by nitrogen dioxide have been studied in a vacuum apparatus connected with an automatic photocolormeter for recording the utilization of nitrogen dioxide and a membrane manometer with a photorecorder on a rotating drum to register the increase in pressure. The cylindrical reaction vessel with soldered plane parallel plates was of quartz ( $d = 45$  mm,  $h = 235$  mm) in the case of methane, and of molybdenum glass ( $d = 50$  mm,  $h = 200$  mm) in the case of propane. The reactor was placed in a tubular electric oven with a constant temperature for the length of the reactor and a horizontal opening for visual observation. The temperature of the oven was maintained by a thermoregulator and was measured with a thermocouple on the outer wall of the reactor. The purity of the methane (not below 99.5%) and of the propane (not below 99.8%) was determined chromatographically. In running the reaction, a previously prepared mixture of the alkane with nitrogen dioxide, allowing for the degree of dissociation of  $N_2O_4$ , was drawn from the preparation flask into the reactor.

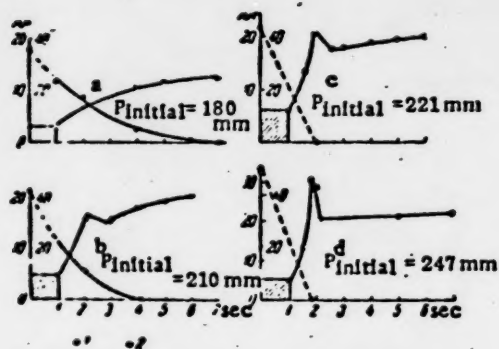


Fig. 1. Three types of kinetic curve. Mixture  $4CH_4 + NO_2$ ,  $475^\circ$ . a — slow reaction, b, c, — reactions with peaks, d — reaction with combustion. Shaded and dotted lines show the area affected by the inertia of the recording apparatus. 1 —  $P_{NO_2}$ , 2 —  $\Delta P$ .

We found three forms of reaction behavior, depending on composition of the mixture, initial pressure, and temperature.

a) Slow reaction (Figs. 1a, 2a). This is characterized by a continuous increase in total pressure up to saturation. At the same time we find a corresponding and also continuous expenditure of  $NO_2$ . The characteristic of the kinetics is a constant rate of expenditure of  $NO_2$  until 30-50% of it is used up (Fig. 2a). In the case of propane at lower temperatures ( $250-300^\circ$ ), small initial pressure, and composition of the mixture  $C_3H_8 : NO_2$  of 1:1, 2:1, and 4:1, the curve of increase in pressure has an S-form (Fig. 2a) and at the beginning of the reaction (sometimes in 30-40 sec.) the total pressure remains almost constant, though a rapid use of  $NO_2$  is observed in this period. This can be explained by the occurrence of a reaction in the initial stages without change in volume. In the case of the reaction of methane with  $NO_2$  such a constant total pressure in the initial moments of the reaction is not observed.

b) Reaction with peak (Figs. 1b, 1c, 2c). With increase in initial pressure or temperature and constant composition of the mixture, the "slow reaction" changes to the "reaction with peak." After a time interval which varies depending on initial conditions from 1.5 to 7 sec. and during which the reaction begins spontaneously, there is a rapid jump in pressure at which time, depending on the height of the peak, there occurs almost complete or very considerable utilization of the  $NO_2$ . The jump in pressure is not connected with the appearance of a visible flame.

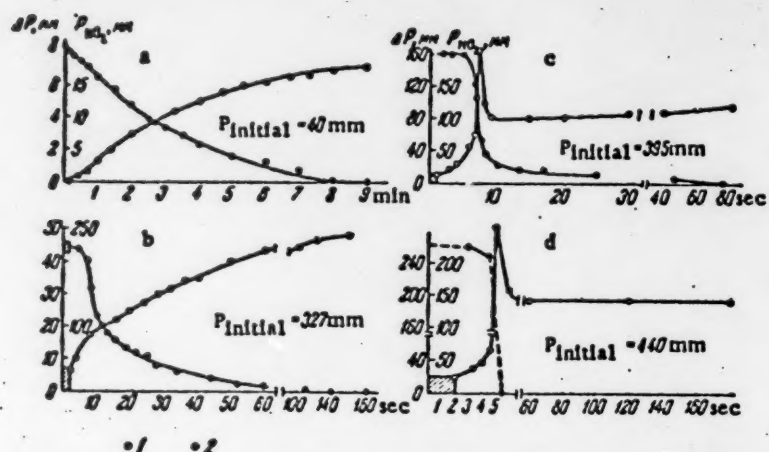


Fig. 2. Three forms of the kinetic curves. Mixture  $C_3H_8 + NO_2$ , 300°. a) slow reaction, b) reaction at the boundary of slow reaction and reaction with peak, c) reaction with peak, d) reaction with combustion. Designations the same as in Fig. 1.

TABLE 1

Composition of the Main Carbon-Containing Products at the Moment of Utilizing the  $NO_2$  for the Three Kinetic Types (in mm mercury of used  $C_3H_8$ )

Conditions	$\frac{RCHO + CO_2 + CO}{RNO_2}$	$\frac{CH_4 + C_2H_6}{RNO_2}$
<b>Slow reaction</b>		
$C_3H_8 + NO_2$ , 300°, $P_{\text{ini.}}$ 327 mm*	$\frac{1,4+6,4+6,4}{13,7} = 1,0$	$\frac{2,7+0}{13,7} = 0,20$
$C_3H_8 + 2NO_2$ , 300°, $P_{\text{ini.}}$ 320 mm*	$\frac{0,9+4,7+8,9}{23,8} = 0,61$	$\frac{0,9+0,9}{23,8} = 0,10$
<b>Reaction with peak</b>		
$2C_3H_8 + NO_2$ , 350°, $P_{\text{ini.}}$ 318 mm*	$\frac{2,7+2,0+3,8}{11,9} = 0,71$	$\frac{1,3+2,0}{11,9} = 0,27$
$C_3H_8 + NO_2$ , 300°, $P_{\text{ini.}}$ 395 mm*	$\frac{3,7+5,5+8,9}{11,0} = 1,6$	$\frac{1,1+2,2}{11,0} = 0,30$
<b>Reaction with combustion</b>		
$C_3H_8 + 2NO_2$ , 350°, $P_{\text{ini.}}$ 171 mm*	$\frac{0,5+2,3+12,4}{0,1} = 150$	$\frac{9,6+12,6}{0,1} = 220$
$C_3H_8 + NO_2$ , 300°, $P_{\text{ini.}}$ 440 mm*	$\frac{7,5+5,2+15,3}{0,9} = 30$	$\frac{9,1+28,0}{0,9} = 40$

\* Initial pressure of the mixture.

Following the jump in pressure, the pressure drops sharply, sometimes (in the case of propane) to the initial pressure, after which there is a further slow rise in pressure to saturation. In Fig. 2b is shown the kinetic curve for the reaction at the boundary of the "slow reaction" and the "reaction with peak."

c) Reaction with combustion (Fig. 1d, 2d). With still greater increase in initial temperature and pressure the spontaneous heating of the reaction leads to an obviously explosive process. In this case the reaction is practically ended in the flame, at which time all the  $NO_2$  is used. The intensity of the flash in this form of the reaction increases at constant temperature as the initial pressure increases and the color changes from a pinkish-blue



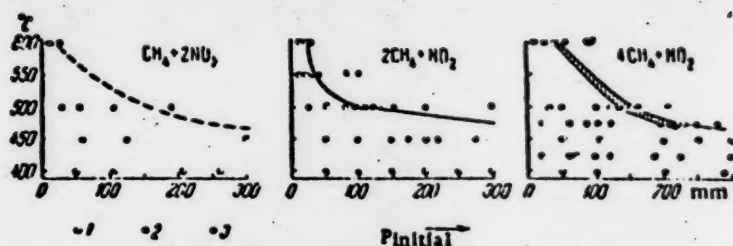


Fig. 3. Fields of the three types of the kinetics of nitration of methane. 1) slow reaction, 2) reaction with peak, 3) reaction with combustion.

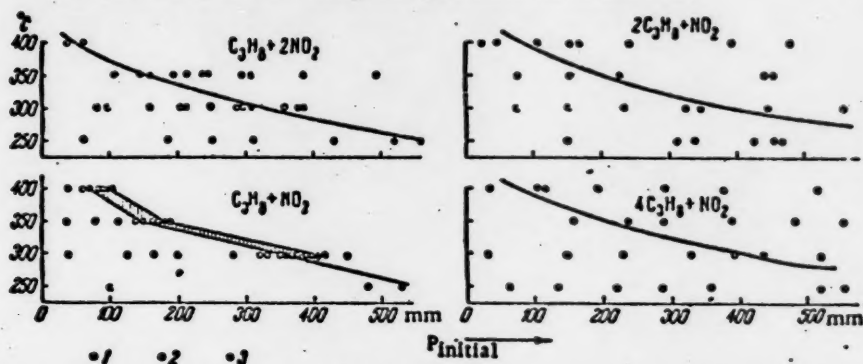


Fig. 4. Fields of the three types of kinetics of nitration of propane. Designations the same as in Fig. 3.

to a whitish-yellow. At lower initial pressure there occurs an expansion of a front of light from the center of the reactor, where the reaction mixture is introduced, to the walls. The rate of expansion in this case is 15-20 cm/sec. The weak light near the boundary of the visual field can be seen only in a dark room; it is like the cold flame of the slow oxidation of hydrocarbons. We did not succeed in observing luminescence visually, that is, the nonexpanding light mentioned by Joffe [1].

The ratio of the increase in pressure at the moment of utilization of  $\text{NO}_2$  to the initial pressure of  $\text{NO}_2$  in the mixture  $\Delta P/P_{\text{initial NO}_2}$  for the reaction between  $\text{CH}_4$  and  $\text{NO}_2$  in the limits of a given mixture does not depend on the type of kinetic reaction, initial pressure, and temperature, and is slightly changed with the composition of the mixture. For the compositions 2:1, 4:1, and 6:1, this ratio is 0.41, 0.43, and 0.36.

The ratio  $\Delta P/P_{\text{initial NO}_2}$  for the reaction between  $\text{C}_3\text{H}_8$  and  $\text{NO}_2$  is determined by the type of kinetic reaction and the composition of the mixture. This ratio is minimal for the reaction with an intense peak (0.14 for 2:1, 400°; 0.12 for 2:1, 350°; 0.04 for 4:1, 400°), maximal for the reaction with combustion (0.75-0.87 for 1:1 and 1:2) and has an intermediate value for the slow reaction (0.22-0.30 for 2:1 and 4:1 and temperatures from 250-400° and 0.38-0.46 for 1:1 and 1:2 and temperatures from 250 to 400°).

As the data of Table 1 show, the composition of the products of the slow reaction and the reaction with peak are close to each other, but differ considerably from the composition of the product from the reaction with combustion.

In Figs. 3 and 4 are given the boundaries of the fields of the different kinetic types. The boundaries of the field of the reaction with peak for  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$  narrow with increase in temperature and with enrichment of the mixture in  $\text{NO}_2$ . Thus, for example, for a composition  $\text{CH}_4 + 2\text{NO}_2$  (400-600°) the reaction with peak was not found, for a composition  $2\text{CH}_4 + \text{NO}_2$  (500°) the reaction with peak occurs in the field  $P_{\text{initial}} = 99-102$  mm, and for the composition  $4\text{CH}_4 + \text{NO}_2$  (500°), in the field  $P_{\text{initial}} = 195-247$  mm.

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# THE ANALYSIS OF FLUOROORGANIC COMPOUNDS. SIMULTANEOUS MICRODETERMINATION OF FLUORINE AND NITROGEN IN ORGANIC COMPOUNDS

N. E. Gel'man, M. O. Korshun, M. N. Chumachenko, and N. I. Larina

(Presented by Academician M. I. Kabachnik, July 8, 1958)

In earlier published work it was established [1, 2] that in the elementary analysis of fluoroorganic compounds magnesium oxide is a reliable reagent for quantitative binding of fluorine liberated in the decomposition of organic substances. It was shown the same time that fluorine absorbed by magnesium oxide could be quantitatively liberated from the layer of absorbent in the form of HF by hydrolytic decomposition of the magnesium fluoride by steam at high temperature [3]. The high temperature hydrolysis, or pyrohydrolysis goes by the following scheme:



On the basis of this fact, we considered it possible to work out a simultaneous determination of fluorine and nitrogen from the same sample by placing magnesium oxide in the zone of decomposition of the substance in the Dumas determination of nitrogen, taking up the fluorine by the magnesium oxide, and then pyrohydrolyzing the magnesium fluoride which was formed. For this purpose we used the modification of the microdetermination of nitrogen by the Dumas method which was worked out by M. O. Korshun and M. N. Chumachenko and was used for the analysis of hard-to-burn compounds; in this they used pyrolytic burning of the sample in a layer of nickel oxide

TABLE 1

Burning in a Layer of Pure Nickel Oxide

Substance	Weight, g	F, %		
		Calculated	Found	Difference
$\alpha$ -Hydroperfluorobutyric anilide $\text{C}_{12}\text{H}_7\text{F}_9\text{NO}$	7,000	42,04	39,63	- 2,41
	4,790		41,06	- 0,98
Tri-( <i>m</i> -nitrophenyl)-oxonium borofluoride $\text{C}_{18}\text{H}_{15}\text{BF}_4\text{N}_3\text{O}_7$	5,200	16,20	15,74	- 0,46
1-Bromo-2(trifluoromethyl)-1,1,3,3,3- pentafluoropropane* $\text{C}_3\text{HBrF}_6$	6,720	54,09	28,09	- 26,00
	4,690		21,67	- 32,42

\* B. p. 56°.

This variant was chosen because pyrolytic burning according to M. O. Korshun [4], carried out in a quartz apparatus, not only assures quantitative combustion, but permits easy replacement of the preparation which absorbs the fluorine after each experiment. The presence of nickel oxide as well as magnesium oxide in the zone of decomposition does not hinder the pyrohydrolytic determination of fluorine, since nickel fluoride is hydrolyzed at a lower temperature than is magnesium fluoride [5]. At the same time, nickel oxide itself at high temperatures does not hold back fluorine completely. In Table 1 are given the results of determining fluorine when the sample was burned in a layer of pure nickel oxide. Combustion was carried out at 900° in an electric furnace 6 cm long.

TABLE 2

Determination of Fluorine and Nitrogen in One 3.5-8 mg Sample

Substance	N, %			F, %			Remarks
	Calculated	Found	Difference	Calculated	Found	Difference	
$\delta$ -(p-fluorophenyl)- $\beta$ -alanine $C_9H_9FNO_2$	7.64	7.67 7.55	+ 0.03 - 0.09	10.37	10.12 10.39	- 0.25 + 0.02	
Trifluoroacetone 2,4-dinitro- phenylhydrazone $C_9H_7F_3N_2O_4$	19.18	19.10 19.20	- 0.08 + 0.02	19.52	19.71 19.88	+ 0.19 + 0.36	
$\beta$ -Trifluoromethyl- $\gamma$ -piperidino- trifluoropropenylbenzene $C_{11}H_{13}F_6NO$	5.53	5.35 5.38	- 0.18 - 0.15	30.02	29.99 29.69	- 0.03 - 0.33	Pyro- hydroly- sis carried out in a nickel tube
N-( $\alpha$ -Trifluoromethyl- $\beta$ -phenyl- 1-trifluoropropenyl)- piperidine $C_{15}H_{15}F_6N$	4.34	4.43 4.32	+ 0.09 - 0.02	35.29	35.66 35.60	+ 0.37 + 0.31	
$\alpha$ -Hydroperfluoroisobutyric anilide $C_{10}H_7F_5NO$	5.16	5.08 5.14	- 0.08 - 0.02	42.04	42.14 42.24	+ 0.10 + 0.20	
p-Toluidine salt of phenyl- fluorophosphinic acid $C_{13}H_{13}FNO_2P$	5.24	5.15 5.26	- 0.09 + 0.02	7.10	7.15 6.94	+ 0.05 - 0.16	
Difluorochloroacetanilide $C_8H_6ClF_2NO$	6.81	6.94 6.84	+ 0.13 + 0.03	18.49	18.39 18.69	- 0.10 + 0.20	
Tri-(m-nitrophenyl-oxonium borofluoride $C_{12}H_{15}BF_6N_3O_7$	8.89	8.76 8.82	- 0.13 - 0.07	16.20	16.09 16.51	- 0.11 + 0.31	Pyrohy- drolysis carried out in a pla- tinum tube
$\alpha$ , $\beta$ , $\beta$ , $\beta$ -Tetrafluoropropio- phenone-2,4-dinitrophenyl- hydrazone $C_{15}H_{13}F_4N_2O_4$	14.51	14.65 14.70	+ 0.14 + 0.19	19.43	19.85 19.57	+ 0.42 + 0.14	
$\alpha$ -Hydro- $\beta$ -methoxyper- fluoropropionitrile* $C_4H_5F_3NO$	10.15	10.13 10.28	- 0.02 + 0.13	40.98	41.02 40.97	+ 0.04 - 0.01	
$\alpha$ -Hydroperfluoroisobutyric acid piperidide $C_9H_{11}F_5NO$	5.32	5.27 5.36	- 0.15 + 0.04	43.31	43.19 43.09	- 0.12 - 0.22	

\*B. p. 106°

For simultaneous determination of fluorine and nitrogen a 3-8 mg sample was placed in a 9 cm long quartz combustion tube filled with a granulated preparation of nickel oxide which contained 15-20 weight % MgO, and this tube was inserted in a larger combustion tube; combustion was carried out at 900-950° in a CO<sub>2</sub> atmosphere. Liquid samples were taken up in thick-walled quartz capillaries which were also placed in the tube and covered with oxidizer. At the end of the combustion of the substance and after the nitrogen had been driven into the azotometer, the contents of the quartz tube were poured into the pyrohydrolytic tube, designed by N. E. Gel'man and K. I. Glazova, through which steam was passed at 1000° at a rate of 0.5 ml of condensate per minute. The pyrohydrolysis lasted 20-25 minutes. Fluorine was titrated in the condensate by thorium nitrate [6] and nitrogen

\* Translation of Russian - Publisher's note (Means nitrogen meter).

was determined by the volume collected in the azotometer. Either a platinum or a nickel tube was used for the pyrohydrolysis. In work with the nickel tube we introduced an empirical correction for the loss of fluorine in the apparatus during pyrohydrolysis.

Nitrogen was determined with an accuracy to 0.2%, fluorine to 0.5%. The results of the analyses of pure substances are given in Table 2.

The determination of fluorine and nitrogen in one sample of organic substance has been carried out first by us.

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\*Original Russian pagination. See C. B. Translation.

\*\*In Russian.



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# THE PREPARATION OF CARBOXYMETHYLCELLULOSE FOR BLOOD-SUBSTITUTE SOLUTIONS

K. F. Zhigach, M. Z. Finkel'shtein, I. M. Timokhin, and A. I. Malinina

(Presented by Academician A. V. Topchiev July 3, 1958)

The sodium salt of carboxymethylcellulose (Na-CMC) was first used as a plasma substitute by Hueper [1]. According to his data, the injection of even great excess amounts of Na-CMC (up to 600 ml of a 0.25% solution per kg) causes no appreciable change in blood composition in the organs of animals. However, when Na-CMC was injected, Hueper found a hypotensive effect which forced him to assume that this preparation had general undesirable characteristics.

Since preparations of CMC can be obtained with different values for the degree of polymerization (DP) and degree of etherification (DE), [2], it seemed desirable to obtain such preparations which might have satisfactory hemodynamic properties.

TABLE 1

Change in DE of CMC Depending on DP of the Alkali Cellulose

Exper. No.	DP of alkali cellulose	Ratio $C_6H_{10}O_5 : CH_2ClCOONa$ (in moles)	DE of CMC
1	315	1:1,35	71,0
2	215	1:1,35	73,0
3	170	1:1,35	77,6
4	116	1:1,30	75,2
5	100	1:1,25	75,3

TABLE 2

Relation of DP of CMC to Duration and Temperature Regime of Pretreatment of Alkali Cellulose

Preparation No.	Conditions of pretreatment	DP of CMC
1	100 hours at 20°	270
2	12 hours at 50° + 32 hours at 20°	130
3	12 hours at 55° + 32 hours at 20°	125
4	17 hours at 50° + 32 hours at 20°	120

Note. Mercerization was carried out with solutions of NaOH (230-235 g/liter) at 20° for 1.5 hours. The alkali cellulose was given preliminary shredding for 2.5 hours at 50° (in exp. No. 1, at 35°).

This work was begun in the Moscow Petroleum Institute in cooperation with the Central Institute for Hematology and Blood Transfusion (TsOLIPK) in 1953.

We synthesized more than 40 different preparations of CMC which were studied as blood-substitute solutions by TsOLIPK.

The degree of CMC polymerization was determined by the method of Wurz [3] and the degree of etherification by iodometric determination of copper salt of CMC.

The DP of the starting cellulose was determined by the specific viscosity of its solutions in quaternary ammonium bases [4].

CMC preparations with different values for DE and DP were obtained by etherification of shredded alkali cellulose with sodium monochloroacetate after first squeezing out the excess alkali solution. The degree of etherification was regulated by changing the ratio of etherifying reagent and cellulose [2], and the DP by the temperature regime and duration of preliminary treatment of the alkali cellulose.

TABLE 3

Breakdown of Alkali Cellulose in the Presence of Hydrogen Peroxide

Preparation No.	Amount of $H_2O_2$ in the mercerization bath		Amount of $H_2O_2$ added to shredder, % wt. of cellulose	Conditions of pretreatment	DP of CMC
	Concn. of $H_2O_2$ in the alkali, %	$H_2O_2$ , % wt. of cellulose			
5	1,5	45	—	3 hours at 40°	167
6	1,5	45	—	6 hours at 40°	130
7	1,5	45	—	5 hours at 45°	130
8	1,5	45	1,5	4 hours at 40°	140
9	—	—	3,5	4 hours at 40°	110
10	—	—	3,5	4 hours at 45°	100

Note. Mercerization was carried out at 35° for 1.5 hours; shredding of the alkali cellulose at 37° for 2.5 hours.

TABLE 4

Change in Functional Groups in Cellulose during the Process of Oxidative Destruction

Preparation No.	Quantity of glucose residues in one group	
	-COOH	-COH
5	89	554
8	75	585
9	73	394
10	69	235

The amount of etherifying reagent needed to obtain the desired degree of etherification depended on the DP of the initial alkali cellulose.

The data of Table 1 show that with decreasing DP of the alkali cellulose with the same ratio of reagents, a higher value for the degree of etherification is obtained (experiments No. 1-3). It was also shown that the desired DE can be obtained with less cost of sodium monochloroacetate by lowering the DP of the starting alkali cellulose (experiments No. 4 and 5).

Only chemically pure preparations of CMC are suitable for making blood-substitute solutions. We used the following method for the purification of CMC pre-

parations. The preparation was precipitated from water solution by alcohol and filtered, then treated with a 5% alcoholic solution of hydrochloric acid. The iron compounds which dissolved in the acid were removed by successive filtration and washing of the resulting cellulose-glycolic acid; this was then dissolved in aqueous alkali, reprecipitated by alcohol, and washed from contaminants by extraction. This process of purification did not change the DP of the CMC and assured a preparation with a high degree of purity.

TABLE 5

Effect of Duration of Hydrolysis of CMC by HCl Solutions on the Blood-Substituting Properties of the Preparations

Preparation No.	DP of starting CMC	Duration of CMC hydrolysis, min	DP of CMC after hydrolysis	Results of biological study
2	130	80	80	+
3	125	75	80	+
6	130	75	90	+
7	130	80	80	+
11	130	85	67	+
12	250	300	70	-
13	240	300	60	-

To assure full solubility, the DE of the CMC should be high. However, the experiments with our CMC preparations in the TsOLIPK showed that variation in DE from 70 to 85 did not affect the actual blood-substituting properties of the CMC [5].

In order to study the effect of DP we prepared a series of samples of CMC with DP from 240 to 58. The most effective were the preparations of CMC with a viscosity of 3.5-5.0 centipoises in 3% water solutions, which corresponds to DP of 70 to 100. Higher molecular weight preparations and also preparations with a lower DP had poor hemodynamic properties. This fact does not agree with the results of G. M. Miklavskaya and E. D. Buglov [6] who used higher molecular weight CMC preparations as blood substitutes.

Of greater significance is the choice of a satisfactory process for obtaining CMC preparations with a low degree of polymerization. Low polymerization of carboxymethylcellulose can be attained by preliminary breakdown of the starting cellulose, or of the alkali cellulose, and by supplementary splitting of the already prepared CMC.

As our investigations showed, preliminary splitting of cellulose by aqueous HCl produces a series of technological difficulties in the mercerization of the cellulose and its further use, and so cannot be recommended.

Oxidative breakdown of the alkali cellulose by oxygen of the air, as Table 2 shows, is a very long process even at raised temperature of pretreatment of the alkali cellulose.

In order to hasten the process of breakdown of the alkali cellulose we used the addition of hydrogen peroxide in the mercerization bath or on the alkali cellulose during its shredding.

The results of the experiments are given in Table 3.

The CMC samples prepared from alkali cellulose split by the use of  $H_2O_2$  behaved differently when studied as blood substitutes: Introduction of small amounts of hydrogen peroxide (up to 1.5% in the shredder and mercerization bath) had no harmful effect on the blood-substituting properties of CMC. Preparations No. 5-8 obtained in this way gave satisfactory results in animals. Addition of larger amounts of  $H_2O_2$  directly on the alkali cellulose during shredding produced toxic properties in the CMC preparations; preparations No. 9-10 caused death when injected into animals.

The results of a chemical investigation of the composition of cellulose which had been submitted to oxidative breakdown are given in Table 4 and show that preparations No. 9 and 10 which caused the death of the animals differ little from preparations No. 5 and 8 in content of carboxyl groups as determined by the O-nitrophenolate method [7]. The content of aldehyde groups, determined by the iodine number [8], is slight in all the preparations (considering their degree of polymerization). In determining the content of carbonyl groups by the hydroxylamine method [9], practically no change in the pH of the solution was observed. Hence, ketone groups are also absent in the samples of cellulose which we studied.

Therefore, the increase in toxic properties in preparations No. 9 and 10 cannot be explained by change in the average chemical composition of the cellulose. Most probably it is due to uneven processes of breakdown and also the accumulation of some quantity of strongly oxidized cellulose which gives the toxic properties to the CMC preparations. We can conclude from this that the use of hydrogen peroxide to hasten the breakdown processes in the alkali cellulose and attain the desired DP should be applied very cautiously.

To obtain a CMC with a DP value below 100 we have carried out a further breakdown of the prepared product by hydrolytic splitting with aqueous hydrochloric acid at 65-70°. The duration of the hydrolysis depends on the initial DP of the CMC preparation.

The experimental use of a high molecular weight CMC preparation (DP 250) for this purpose gave unsatisfactory results: preparations No. 12 and 13, obtained by this process, are toxic, as Table 5 shows, while the samples obtained from further destruction of comparatively low molecular weight CMC preparations (DP about 130) give positive results.

The negative results are evidently due to hydrolytic splitting of high molecular weight CMC preparations in a heterogeneous medium; some of the highest molecular weight fractions remain insufficiently broken down and this is reflected harmfully in the blood-substituting properties.

This investigation will permit us to plan a technical method for obtaining Na-CMC preparations which have blood-substituting properties.

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# A STUDY OF THE MECHANISM OF THE SPONTANEOUS DECOMPOSITION OF POTASSIUM OZONIDE BY THE USE OF A MAGNETIC METHOD

Corresponding Member AN SSSR I. A. Kazarnovskii, S. I. Raikhshtein and  
L. N. Bykova

A study of the kinetics of the spontaneous decomposition of potassium ozonide [1] has shown that this reaction proceeds according to the equation



and has an autocatalytic character with an induction period at 18, 0, -9, and -18° corresponding to 1.67, 20, 54, and 205 days. In the following active period the rate of splitting of potassium ozonide increases rapidly; the energy of activation is 22-23 kcal/mole.

TABLE 1

Experiment No. 15, Preparation No. 1, Sample 0.5463 g, Temperature 19°

No.	Time from start of experiment, hours	Degree of decomposition of $\text{KO}_3$ , from oxygen formed, %	Gram magnetic susceptibility			
			$\chi_g \cdot 10^4$			
			Measured	Corrected	Calculated by additivity rule*	$\Delta$ , %
1	0	0	+15.15	+16.89	—	—
2	17	8.1	+15.95	+17.81	+17.60	+1.2
3	23	9.5	+15.90	+17.76	+17.70	+0.3
4	41.5	11.1	+16.10	+17.98	+17.80	+1.0
5	47.5	18.9	+17.60	+19.67	+18.09	+8.7
6	67.3	27.4	+20.30	+22.75	+19.20	+18.5
7	89.5	48.8	+22.50	+25.33	+21.02	+20.5
8	94.5	56.3	+23.15	+26.11	+21.64	+20.7
9	113.5	74.2	+23.50	+26.62	+23.17	+14.9
10	118.5	78.3	+23.20	+26.31	+23.51	+11.9
11	161.5	95.0	+23.05	+26.25	+24.96	+5.2
12	167.5	96.1	+23.15	+26.38	+25.08	+5.2
13	186.5	98.1	+22.70	+25.88	+25.22	+2.6
14	191	98.1	+22.75	+25.93	+25.22	+2.8
15	220	100	+22.30	+25.44	—	—
16	230	100	+22.20	+25.33	—	—

\*Calculated by the equation:  $\chi_g(\text{mixture}) = a \chi_g(\text{KO}_3) + (1-a) \chi_g(\text{KO}_2)$ , where  $a$  is amount of potassium ozonide in the mixture.

In order to explain the mechanism of the decomposition of potassium ozonide, we have undertaken magnetic measurements. In the formation of a strongly paramagnetic intermediate product we can expect a shift of the magnetic susceptibility with additivity toward an increase; in the case of formation of a diamagnetic product, toward a decrease.

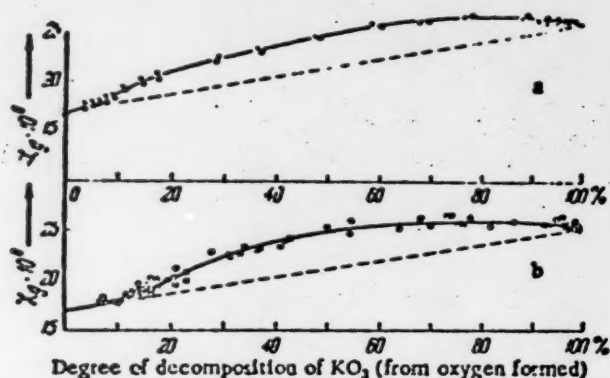


Fig. 1. Change in magnetic susceptibility during decomposition of  $\text{KO}_3$  at  $0^\circ$  (a) and at  $18-20^\circ$  (b)

TABLE 2

Amount of Atomic Oxygen in the Solid Reaction Product of Decomposition of Potassium Ozonide (Experiment No. 15)

No.	Time from beginning experiment, hrs.	Degree of $\text{KO}_3$ decomposition, from oxygen formed, %	Weight of solid reaction products (g), g	Amount of $\text{KNO}_3$ (x), g.	Amount of $\text{KNO}_3$ (y), g	Amount of atomic oxygen (z), g	True degree of decomposition of $\text{KO}_3$ , %	Amount of atomic oxygen, g-at	
								Per 100 moles starting $\text{KO}_3$	Per 100 moles decomposed $\text{KO}_3$
1	0	0	0.4901	0.4901	—	—	—	—	—
2	17	8.1	0.4828	0.4461	0.0357	0.0003	9.0	0.9	9.9
3	23	9.5	0.4815	0.4408	0.0402	0.0005	10.1	0.6	5.5
4	41.5	11.1	0.4801	0.4319	0.0473	0.0006	11.8	0.7	5.6
5	47.5	13.9	0.4775	0.4013	0.0724	0.0037	18.2	4.1	22.7
6	67.3	27.4	0.4654	0.3134	0.1441	0.0077	36.4	8.5	23.7
7	89.5	48.8	0.4461	0.2013	0.2357	0.0090	60.3	10.0	16.9
8	94.5	56.3	0.4393	0.1636	0.2664	0.0091	65.3	10.1	15.2
9	113.5	74.2	0.4231	0.0883	0.3279	0.0067	81.9	7.5	9.1
10	118.5	78.3	0.4195	0.0758	0.3481	0.0055	84.4	6.0	7.2
11	161.5	95.0	0.4044	0.0109	0.3911	0.0022	97.9	2.5	2.5
12	167.5	96.1	0.4034	0.0054	0.3957	0.0023	99.3	2.5	2.6
13	186.5	98.1	0.4016	0.0023	0.3982	0.0011	100	1.2	1.3
14	191	98.1	0.4016	0.0018	0.3986	0.0012	100	1.4	1.4
15	220	100	0.3988	—	0.3986	—	100	—	—
16	230	100	0.3988	—	0.3986	—	100	—	—

The potassium ozonide preparation contained 88-92%  $\text{KO}_3$ . As an example, we give preparation No. 1:  $\text{KO}_3$  89.8%,  $\text{KOH}$  8.0%,  $\text{H}_2\text{O}$  (in the form of  $\text{KOH} \cdot \text{H}_2\text{O}$ ) 2.2%.

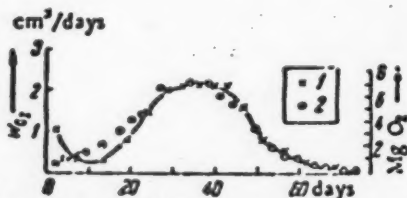


Fig. 2. Rate of evolution of molecular oxygen (1) and amount of atomic oxygen (2). Temperature  $0^\circ$ . (Experiment No. 16).

The magnetic measurements were carried out at the same time as the kinetic ones, at room temperature ( $18-20^\circ$ ) and at  $0^\circ$ . The measurements were made by the Gouy method in an apparatus with a large laboratory electromagnet. A sample of 0.5-0.6 g of potassium ozonide powder was placed in a Jena glass ampule, diameter about 2 mm and length 140 mm, joined to a stopcock and ground glass joint which permitted alternate connection of the ampule to the magnetic apparatus and to a gas buret in which the amount of oxygen which formed was measured. Before it was filled, the ampule was ignited in a vacuum to remove adsorbed moisture.

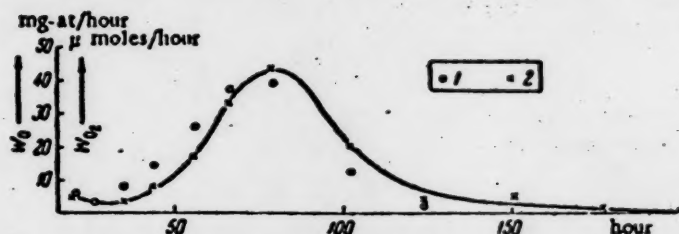


Fig. 3. Rate of formation of atomic oxygen (1) and evolution of molecular oxygen (2). Temperature 19-20°. (Experiment No. 22).

The operations of taking the sample and filling the ampule were carried out in a special dry chamber. The variations in weighing the ampule on the magnetic balance did not exceed 0.09 mg while the change in weight of the samples in the magnetic field was 15 to 45 mg. The results of the magnetic measurements with different preparations, as a rule, were reproducible within  $\pm 2\%$ .

In all, we carried out nine experiments: seven at 18-20° and two at 0°.

The initial product  $\text{KO}_2$  and the final  $\text{KO}_2$ , as is known, are paramagnetic. At room temperature our potassium ozonide preparation gave  $\chi_g \cdot 10^6 = +16.9 \pm 0.15$  and the final product (potassium superoxide) gave  $\chi_g \cdot 10^6 = +25.2 \pm 0.15$ . These values, calculated to 100% preparations\*, are in satisfactory agreement with the previous data [2-4].

In Table 1 and in Fig. 1 are given the results of some kinetic and magnetic measurements at room temperature and at 0°. The dotted straight lines give the values of  $\chi_g$  calculated by the rule of additivity.

The observed variation from additivity, which is far beyond the limits of experimental error, indicates the intermediate formation of a strongly paramagnetic product. It is natural to assume that this product is atomic oxygen whose magnetic susceptibility is several times greater than those of  $\text{KO}_2$  and  $\text{KO}_3$ , since the atom of oxygen in the ground state ( $^3P$ ) has two unpaired electrons.

The intermediate formation of oxygen atoms is confirmed also by the observation of the formation of traces of ozone which is shown by oxidation of the mercury surface in the manometer apparatus.

The amount of atomic oxygen in different stages of the process can be estimated from the magnetic data and the weight of the solid product of the reaction. From the fact that the latter consists of  $\text{KO}_2$ ,  $\text{KO}_3$ , and oxygen, we can set up three equations:

$$x + y + z = g_t \quad (1)$$

$$0.4489x + 0.5499y = 0.4489g_0 \quad (2)$$

$$\chi_g(\text{KO}_2)x + \chi_g(\text{KO}_3)y + \chi_g(\text{O})z = g_t\chi_g(\text{mixture}) \quad (3)$$

where  $g_0$  is the amount of  $\text{KO}_2$  in the starting sample,  $g_t$  the weight of solid reaction product,  $x$  the amount of  $\text{KO}_2$ ,  $y$  the amount of  $\text{KO}_3$ , and  $z$  the amount of atomic oxygen in time  $t$  hours (weights in grams);  $\chi_g(\text{KO}_2)$ ;  $\chi_g(\text{KO}_3)$ ;  $\chi_g(\text{O})$  and  $\chi_g(\text{mixture})$  are the gram magnetic susceptibilities at the temperature of the experiment\*\*\*.

\*In calculating the magnetic susceptibilities of the 100% preparations we could neglect the diamagnetism of the mixture of  $\text{KOH}$  and  $\text{H}_2\text{O}$ . This applies also to the corrected values for the gram susceptibility of the solid reaction product in Table 1.

\*\*V. I. Smirnova took part in the measurements.

\*\*\*The magnetic susceptibility of atomic oxygen has not been measured up to now. Theoretical calculation by the van Vleck equation gives for room temperature (293°K) a value of  $\chi_g(\text{O}) \cdot 10^6 = 5000/16 = 312.5$  [5]. Since in our case the orbital component of the magnetic moment is evidently fixed by the lattice ions, then for the susceptibility of atomic oxygen in the solid phase we take the theoretical value which corresponds only to the spin. Then we have at 293°K:  $\chi_g(\text{O}) \cdot 10^6 = 3090/16 = 211.8$ ; at 273°K:  $\chi_g(\text{O}) \cdot 10^6 = 227.5$ . The amounts of atomic oxygen calculated from these values are probably an upper limit.

Equation (2) is based on a constant amount of potassium in the reaction mixture. When we solve equations (1), (2), and (3) with the numerical values  $x_g(KO_3) \cdot 10^3 = +16.89$ ;  $x_g(KO_2) \cdot 10^3 = +25.33$ , and  $x_g(O) \cdot 10^3 = +211.88$ , we find

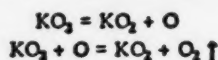
$$\begin{aligned}x &= 4.9484 g_t - 3.5539 g_o - 0.0234 g_t \cdot x_x \text{ (mixture)} \\y &= 3.7175 g_o - 4.0395 g_t + 0.0191 g_t \cdot x_x \text{ (mixture)} \\z &= 0.0911 g_t - 0.1636 g_o + 0.0043 g_t \cdot x_x \text{ (mixture)}\end{aligned}$$

These equations permit us to calculate the amount of  $KO_3$ ,  $KO_2$ , and atomic oxygen in different stages of the decomposition process for  $KO_3$ . In Table 2 we give the results for experiment No. 15.

From the data of Table 2 it follows that at the beginning of the decomposition the content of atomic oxygen in the solid phase rises, passes through a maximum at about 60% decomposition of potassium ozonide, and then falls to zero at 100% decomposition. At the maximum point the solid phase contains as atoms about 15% of all the oxygen formed. The greatest relative amount of atomic oxygen (up to 25%) is found at the end of the induction period or at the beginning of the active period.

This result is an argument for the proposed hypothesis of the nature of the induction period which rests on the theory of defective crystal structure. According to this hypothesis, the induction period is characterized by an accumulation of defects in the crystal lattice of potassium ozonide, that is, ions of  $O_2^-$  and atoms of oxygen; when some critical quantity of these defects is reached, the initial structure decomposes into a phase saturated by the defects and by seeds of the new phase,  $KO_2$ . This moment corresponds to the beginning of the active period of the reaction, which occurs preferably at the boundary of the two phases.

To explain the mechanism of the evolution of molecular oxygen we compared the rate of this process ( $w_{O_2}$ ) with the amount of atomic oxygen in the solid phase ( $z$ ). In Fig. 2 we give as an example the data of experiment No. 16. They show that the formation of molecular oxygen is a first-order reaction with respect to atomic oxygen. This makes a recombination mechanism improbable and indicates a reaction of oxygen atoms with ozonide ions:  $O + O_3^- = O_2^- + O_2$ . Further kinetic analysis shows the same regularities for the rate of formation of atomic oxygen as for the rate of evolution of molecular oxygen, namely, a curve with a clearly expressed topochemical maximum (Fig. 3). Hence both of the main events in the splitting of the ozonide into potassium superoxide and oxygen



proceed preferably at the boundary of the separate phases.

It is possible that an analogous mechanism takes place in the decomposition of other metal oxides and also of salts of oxygen acids. We plan studies with the use of atomic oxygen to test this hypothesis.

L. Ia. Karpov Physicochemical Research Institute.

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## BORON ORGANIC COMPOUNDS

### ALLYL DERIVATIVES OF BORON

B. M. Mikhailov and F. E. Tutorskaia

(Presented by Academician B. A. Kazanskii, July 11, 1958)

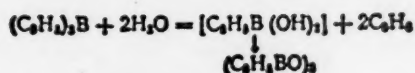
Among the allyl compounds of boron only triallyl boron is known with certainty. The report of Rothstein and Saville [1] on the preparation of other compounds of this series must be regarded critically, as will be clear from our further remarks.

We have studied the chemical properties of triallyl boron and have obtained from it a series of new allyl derivatives of boron.

The triallyl boron which we needed was prepared by the action of allylmagnesium bromide on the etherate of boron fluoride in 68% yield. The preparation had a b. p. 165°, like the triallyl boron obtained in 33% yield from triallyl borate and allylmagnesium bromide [2]. A. V. Topchiev and co-workers [3] obtained triallyl boron with a higher boiling point in the one stage addition of a mixture of allyl bromide and the etherate of boron fluoride to magnesium.

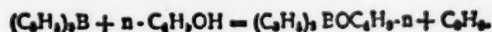
The investigation showed that triallyl boron had a considerably greater reactivity than the triallyl compounds of boron.

In distinction to the latter, it reacted with water at room temperature to form allyl boric acid, isolated as the anhydride



In the first stage of the reaction diallylboric acid evidently formed and this underwent a further hydrolytic splitting at the boron-carbon bond.

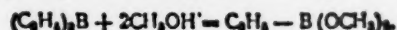
Triallyl boron reacted with alcohols at room temperature. When 1 mole of n-butyl alcohol acted on it, it gave propylene and n-butyl diallylborate



The latter in turn could react with alcohols and so by the action of 2 molecules of alcohol on triallyl boron di-n-butyl allylborate was obtained



By the action of methyl alcohol on triallyl boron at a ratio of reagents 1:1 was obtained, not the methyl ester of diallyl boric acid, but dimethyl allylborate and part of the original triallyl boron was recovered unchanged:

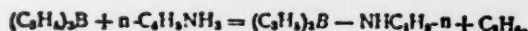




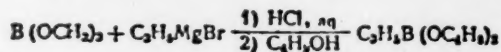
The esters of diallylboric acid are very unstable to water; when it acts on them in the cold they are hydrolyzed to allylboric acid.

Rothstein and Saville [1] claimed that when allylmagnesium bromide acts on boron fluoride with subsequent decomposition of the reaction product by water, the anhydride of diallylboric acid is obtained. Since diallylboric acid, from which the anhydride could be obtained by distillation, is hydrolyzed by water into allylboric acid, then it is apparent that under their conditions these authors could not have obtained this anhydride.

Triallyl boron reacted easily with *n*-butylamine. The reaction occurred at room temperature and with equimolecular quantities of reagents led to the formation of diallyl-*n*-butylaminoboron



We studied further the reaction between allylmagnesium bromide and trimethyl borate. If the reaction product was not decomposed by water, but after removal of the ether the residue was heated in a vacuum, then some liquid distilled over. Fractional distillation established the presence in the distillate of dimethyl allylborate and triallylboron. After decomposition of the dry, bulky residue by dilute hydrochloric acid and esterification of the reaction product with allyl alcohol, we obtained diallyl allylborate. In another experiment, the product of the Grignard reaction was decomposed directly with hydrochloric acid and esterified with *n*-butanol. As a result we obtained a 45% yield of di-*n*-butyl allylborate



According to the data of Rothstein and Saville the reaction of allylmagnesium bromide and methyl borate (1:1) forms methyl diallylborate and a substance which boils at 110°/0.4 mm, which, in the opinion of the authors, is diallyl allylborate. It is known that the authors could not have obtained this compound, since they treated the reaction product with water, while the esters of allylboric and diallylboric acids are easily hydrolyzed to allylboric acid by it. We should say that the substance which the authors took for methyl diallylborate boiled higher (190°) than our *n*-butyl diallylborate (b. p. 185°), and the diallyl allylborate has a b.p. 82°/21 mm and not 110°/0.4 mm.

There is interest in studying the reaction of allylmagnesium bromide with esters of metaboric acid, with which arylmagnesium bromides react to form diarylboric acids [4]. We showed that when allylmagnesium bromide reacted with *n*-butyl metaborate, with subsequent decomposition of the reaction product by water and esterification by *n*-butyl alcohol we obtained dibutyl allylborate (24.8%) and a substance with b. p. 166°/2.5 mm with the same elementary composition as dibutyl allylborate but with double the molecular weight. The structure of this "dimer" was not worked out.

## EXPERIMENTAL

All the operations were carried out in a nitrogen atmosphere.

**Triallyl boron.** To an ether solution of allylmagnesium bromide prepared from 42.5 g (1.77 moles) of magnesium, 70.8 g (0.58 mole) of allyl bromide, and 470 ml of absolute ether in a four-neck flask fitted with a stirrer, dropping funnel, reflux condenser and inlet for nitrogen, was added over 50 min an ether solution of 20.3 g (0.14 moles) of boron trifluoride etherate; the solution was stirred strongly during the addition. The reaction mixture was stirred and refluxed for 3 hours, then allowed to stand overnight. On the next day the ether was poured from the thick layer of salts and the residue was washed with 100 ml of boiling absolute ether. The ether was distilled from the combined extracts. The residue was distilled in a vacuum. We obtained 12.7 g (68.1% of the theory) of triallyl boron with b. p. 44-46°/10 mm;  $d_4^{20}$  0.7689;  $n_D^{20}$  1.4500.

Found %: C 80.85; 80.74; H 11.37; 11.39; B 8.13; 8.09  
 $C_9H_{15}B$ . Calculated %: C 80.65; H 11.28; B 8.07.

**Allylboric anhydride.** To 8.6 g (0.064 mole) of triallyl boron, cooled to -60°, was added 1.15 g (0.064 mole) of oxygen-free water in 4 ml of absolute tetrahydrofuran, with strong stirring and over 1.5 hours. Strong foaming occurred. Then the mixture was stirred for 30 min at room temperature, the tetrahydrofuran was distilled off, and the residue was distilled in a vacuum. We isolated 2.64 g (61% of the theory) of allylboric anhydride

with b. p. 86.5-91°/7 mm. After repeated distillation the substance had b. p. 60.5-61°/3 mm,  $d_4^{20}$  0.9318,  $n_D^{20}$  1.4435.

Found %: C 52.95; 52.97; H 7.19; 7.33; B 16.14; 15.72; M 186.8  
( $C_3H_7BO$ )<sub>3</sub>. Calculated %: C 53.08; H 7.42; B 15.94; M 203.7.

Allylboric anhydride is a mobile liquid which catches fire in air and easily polymerizes when slowly distilled.

**Di-n-butyl allylborate.** To 6.23 g (0.046 mole) of triallyl boron was added over an hour and with strong stirring 6.84 g (0.092 mole) of absolute n-butyl alcohol; the solution grew warm. 3.2 g of propylene condensed in a trap cooled to -75°. When the reaction mass was distilled we obtained 8.05 g (88.4%) of di-n-butyl allylborate with b. p. 98-100°/15 mm,  $d_4^{20}$  0.8413,  $n_D^{20}$  1.4230.

Found %: C 66.60; 66.56; H 11.72; 11.65; B 5.03; 5.29  
 $C_{11}H_{23}BO_2$ . Calculated %: C 66.58; H 11.70; B 5.45.

The ester dissolved in benzene and ether and was easily hydrolyzed by water.

**n-Butyl diallylborate.** To 8 g (0.059 mole) of triallyl boron was slowly added 4.48 g (0.059 mole) of absolute n-butyl alcohol. The reaction was accompanied by heating. Fractionation gave 5.9 g (60.2%) of n-butyl diallylborate with b. p. 60-66°/7 mm. After further distillation, the ester had b. p. 61-62°/6 mm,  $d_4^{20}$  0.8092,  $n_D^{20}$  1.4303.

Found %: C 72.68; 72.48; H 11.28; 11.48; B 6.49; 6.45  
 $C_{10}H_{18}BO_2$ . Calculated %: C 72.32; H 11.53; B 6.51.

The substance was soluble in ether and benzene; water hydrolyzed it to allylboric acid.

In the experiment we also obtained 0.9 g (7.7%) of di-n-butyl allylborate ( $n_D^{20}$  1.4230) and propylene.

**Dimethyl allylborate.** To 14.53 g (0.108 mole) of triallyl boron was slowly added with energetic stirring 3.46 g (0.108 mole) of absolute methyl alcohol. The reaction mixture was distilled. 3.46 g of propylene condensed in the trap (-70°).

When the distillate was fractionated, we obtained as reaction products: 1) 3.9 g of dimethyl allylborate with b. p. 42-43°/60 mm (31.7% of the triallyl boron taken in the reaction),  $d_4^{20}$  0.8671,  $n_D^{20}$  1.4021.

Found %: C 52.82; 52.70; H 9.68; 9.89; B 9.31; 9.28  
 $C_5H_{11}BO_2$ . Calculated %: C 52.70; H 9.73; B 9.49.

2) 3.5 g of triallyl boron, b. p. 76-80°/60 mm.

3) A fraction amounting to 1.4 g with b. p. 117-119°/47 mm (not studied).

**Diallyl-n-butylaminoboron.** To 6 g (0.048 mole) of triallyl boron was added over a period of 30 min 3.28 g (0.0448 mole) of n-butylamine. The mixture grew warm and frothed. Then the mixture was heated for 30 min at 100°. 1.2 g of propylene collected in the trap. After distillation we obtained 5.5 g (74.4%) of diallyl-n-butylaminoboron with b. p. 85.5-86.5°/17 mm,  $d_4^{20}$  0.8338,  $n_D^{20}$  1.4697.

Found %: C 72.83; 72.93; H 12.27; 12.00; B 6.06; 6.45  
 $C_{11}H_{23}BN$ . Calculated %: C 72.74; H 12.21; B 6.55.

The substance dissolved in benzene and ether and was easily hydrolyzed by water.

**Action of allylmagnesium bromide on trimethyl borate.** To a mixture of 52 g (0.5 mole) of trimethyl borate and 200 ml of ether, cooled to -75°, was added over 6 hours an ether solution of allylmagnesium bromide prepared from 42.5 g of magnesium and 70.8 g (0.58 mole) allyl bromide in 470 ml of ether. The reaction mass was stirred for 2 hours and then allowed to stand in a refrigerating bath overnight.

On the next day the ether was distilled from the thick mass of reaction mixture and then the liquid products were distilled off in a vacuum (18 mm). The condensate which collected in the trap (-70°) was fractionated; we obtained 3.9 g (6.8%) of methyl allylborate (b. p. 107-109°,  $n_D^{20}$  1.4022) and 0.36 g of triallyl boron.

The dry residue obtained after distilling off the reaction products was decomposed with 400 ml of 3.5% hydrochloric acid, the ether layer was separated and the water layer was extracted with 200 ml of ether. After distillation of the ether, the residue was esterified with 200 ml of allyl alcohol. After distillation of the azeotropic mixture of allyl alcohol with water and the alcohol, the reaction product came over.

We obtained 26.3 g (31%) of diallyl allylborate with b. p. 81-84°/21 mm. After further redistillation, the substance had a b. p. 82-82.5°/21 mm,  $d_4^{20}$  0.8931,  $n_D^{20}$  1.4352.

Found %: C 64.90; 64.81; H 9.22; 9.47; B 6.27; 6.17  
 $C_9H_{13}BO_2$ . Calculated %: C 65.10; H 9.11; B 6.52

In the water layer we found 41.5% boric acid.

In another experiment the reaction product was hydrolyzed with hydrochloric acid and then esterified with n-butanol. We obtained 45.2 g (45.6%) of di-n-butyl allylborate with b. p. 92-96°/11 mm ( $n_D^{20}$  1.4230), and 12.5 g (10.7%) of tributyl borate with b. p. 104-109°/11 mm. In the water layer we found 36.7% boric acid.

Action of allylmagnesium bromide on n-butyl metaborate. To a solution of 0.93 mole allylmagnesium bromide in 725 ml of ether with strong stirring was added 46.6 g (0.155 mole) of n-butyl metaborate dissolved in 52 ml of benzene. At the end of the spontaneous warming, the mixture was boiled for 2 hours on an air bath and then hydrolyzed with 500 ml of 7% hydrochloric acid. After the ether was distilled off, the residue was esterified with n-butanol. We obtained 22.9 g (24.8%) of n-butyl allylborate with b. p. 90-94°/9.5 mm and 17.6 g (19.1%) of the dimer of n-butyl allylborate with b. p. 165-166°/3 mm;  $d_4^{20}$  0.8814;  $n_D^{20}$  1.4388.

Found %: C 66.55; 66.90; H 11.51; 11.75; B 5.48; 5.31; M 349.7  
 $(C_{11}H_{23}O_2)_2$ . Calculated %: C 66.69; H 11.70; B 5.46; M 396.2.

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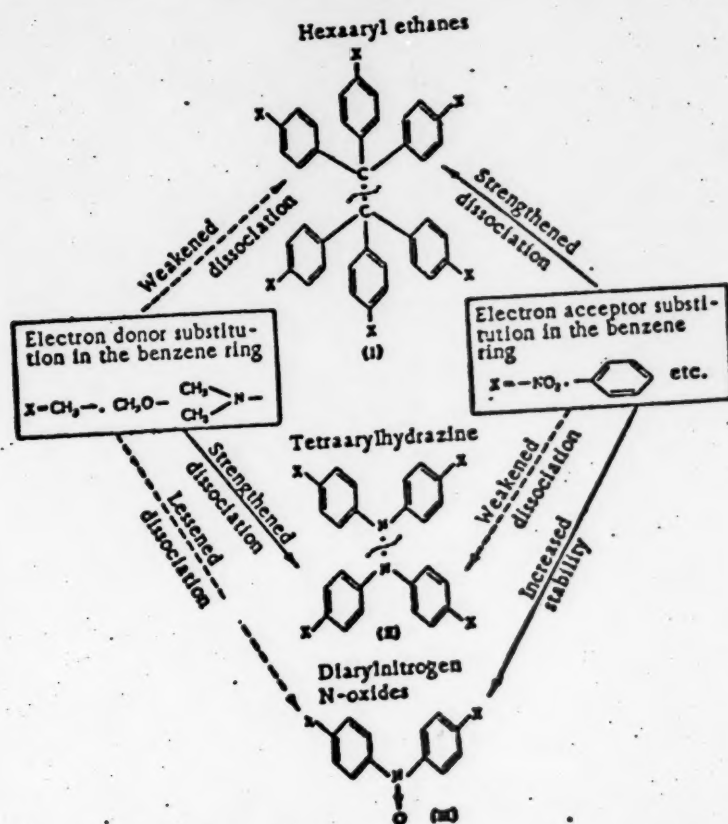
\*Original Russian pagination. See C. B. Translation.

# THE STRUCTURE, PROPERTIES, AND ABILITY TO DISSOCIATE INTO FREE RADICALS OF SOME HYDRAZINE DERIVATIVES. THE QUESTION OF THE RELATION OF CHEMICAL STRUCTURE AND ABILITY TO FORM FREE NITROGEN RADICALS

L. B. Radina, Z. V. Pushkareva, and Z. Iu. Kokoshko

(Presented by Academician I. N. Nazarov, November 20, 1956)

As we have stated in a previous communication [1], the diaryl nitrogens which are formed in the dissociation of tetraarylhazirines with the general formula II belong to the class of free nitrogen radicals.



Radicals of this group were discovered in 1911 and were studied in detail by Wieland and co-workers [2-5], but until now the question has not been settled as to the reason for the facts known from the literature about the contradictory character of the rules for dissociation into free radicals of the molecules of hexaarylethanes (I), tetraarylhazirines



TABLE 1

Name of substance	Half wave potential corresponding to reduction of the N-N bond in the hydrazines in volts on the dropping electrode		$\mu_{\text{exp}} \cdot 10^{18}$
	In acetate buffer, pH 4.25	In ammonia buffer, pH 8.04	
Hydrazine	-1.34	-1.49	1.9
Phenylhydrazine	-0.15	—	—
Hydrazobenzene	-0.20	-0.25	1.85
Tetraphenylhydrazine	-0.61	-0.82	1.27
p, p'-Dinitrophenylhydrazine	-0.93	-0.97	—
Tetra-p-nitrophenylhydrazine	-1.22	-1.64	4.15
p, p'-Dimethoxyhydrazobenzene	-1.27	—	4.27
Tetra-p-anisylhydrazine	-0.62	-0.62	1.30
Diethylhydrazine	—	-0.16	0.51
Tetraethylhydrazine	—	-0.18	1.62
Diacetylhydrazine	-0.13	-0.18	—

(II) and diaryl nitrogen N-oxides (III) in relation to the structure of substituents in the benzene ring (X). The Fig. shows at a glance the interrelations between the nature of the substituting group and the ability to form free radicals in a number of compounds of these types.

TABLE 2

Compound	Half wave potential in volts on dropping electrode		
	X = H	X = OCH <sub>3</sub>	X = NO <sub>2</sub>
	-0.20	-1.27	-0.11
	-0.61	-0.62	-1.22

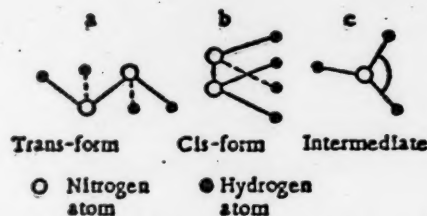
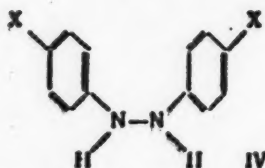


Fig. 1. a and b — the N-N axis lies in the plane of the figure, c — the N-N axis is perpendicular to the plane of the figure.

In order to cast experimental light on the reasons behind these facts, we have studied the chemical transformations, tendency to polarographic reduction, and the dipole moments for a specially selected group of substances of the di- and tetrasubstituted hydrazine series.

The central position among the substances which we studied are occupied by the so-called "model" substances, tetraphenylhydrazine (II, X = H), which dissociates moderately into two molecules of diphenyl nitrogen, tetra-p-nitrophenylhydrazine (II, X = NO<sub>2</sub>), which cannot dissociate into radicals, and tetra-p-anisylhydrazine (II, X = OCH<sub>3</sub>), which has an increased tendency to dissociate into free radicals, and also the substituted diphenylhydrazines of the general formula IV which correspond to them.





All these substances were synthesized by the methods described in the literature [2, 3, 5-10] except for tetraethylhydrazine which was obtained by direct oxidation of diethylamine with potassium permanganate.

As the chief methods of study we chose polarographic reduction on the mercury dropping electrode, which allowed us to characterize the strength of the N-N bond, and the measurement of the dipole moments which answered the question of the spatial configuration of these compounds.

The results of the polarographic reduction of the hydrazine derivatives, measured on a Heyrovsky micropolarograph in acetate and ammonia buffer solutions, are given in Fig. 1.

The following basic observations were made as a result of the polarographic reduction of hydrazine derivatives.

1) All substitutions of hydrazine hydrogens (mono-, di-, or tetra-) make reduction on the dropping mercury electrode easier.

2) Among the diaryl-substituted hydrazines the introduction of an electron acceptor nitro group into the p-position in the benzene ring shifts the half-wave potential to the side of the positive values, that is, it makes reduction of the N-N bond easier. When an electron-donor methoxy group is introduced, the reverse is found — a sharp shift in potential toward the negative values (Table 2).

3) When we turn from the disubstituted hydrazines to the tetrasubstituted ones, we find the effect of the substituents on the strength of the N-N bond is unexpectedly changed: the presence of nitro groups in the p-position of the benzene ring, instead of making the reduction much easier, leads to a shift in half-wave potential toward the negative values, while the introduction of the methoxy group in the same position does not give the expected difficulty of reduction of the N-N bond on the dropping mercury electrode (Table 2). We can assume from these data that in the tetraarylhydrazines, as opposed to the diarylhydrazines, the electron-accepting nitro group and the electron-donor methoxy group are drawn away by some factor from their connection with the p-electron of the central nitrogen atom and do not show their usual electron-acceptor and electron-donor actions.

In order to test this assumption experimentally for some of the compounds we measured the dipole moments. The measurements were made by the beat method in benzene at 25° (see Table 1).

Comparison of the experimental values for the dipole moments with those calculated by the method of vector sums for the three different configurations of hydrazine which are shown schematically in Fig. 1, and a consideration of the spherical model of the molecule permit the discovery of some interesting facts.

It is shown that almost all these hydrazine derivatives, like the simplest hydrazines [11], do not have free rotation of the dipole with respect to the N-N bond and also it would seem do not have the most energetically favorable trans-configuration (Fig. 1, a). Consideration of the model molecule of tetraarylhydrazines shows that the reason for this is the spatial difficulty which occurs in both the cis- and trans-configurations.

The spatial difficulty is particularly clear in the case of tetra-p-nitrophenylhydrazine (II, X = NO<sub>2</sub>). The dipole moments calculated for the cis- and trans-configurations are 6.72 D and 0 respectively, and the experimental dipole moment is 4.15 D.

From this it follows that cis- and trans-configurations of the molecule are impossible here (evidently here there is a considerable repulsive effect of the nitro group), and the only possible configuration of the molecule is the so-called "intermediate" (Fig. 1, c;  $\mu_{\text{calcd.}} = 4.10$  D). The presence of this configuration in turn almost completely excludes the possibility of p- $\pi$ -combination (the axes of the clouds of p- and  $\pi$ -electrons are almost perpendicular). The result is that there is no effect of the nitro group as an electron-acceptor substituent on the N-N bond; the electron density remains the same as in the unsubstituted hydrazine and its reduction on the dropping mercury electrode occurs at a very negative potential ( $E_1$  for hydrazine = -1.36 v;  $E_1$  for tetra-p-nitrophenylhydrazine = -1.22 v), while in p,p'-dinitrophenylhydrazine the nitro groups make the reduction considerably easier.

On this basis we can assume that the inability to dissociate into free radicals of tetra-p-nitrophenylhydrazine is not connected at all with the fact that the electron-acceptor nitro group in tetra-p-nitrophenylhydrazine acts oppositely from its behavior in hexaarylethanes, but is due to spatial factors which prevent p- $\pi$ -combination in the molecule.

In the case of tetra-p-alkylhydrazine (II, X = OCH<sub>3</sub>) there is a configuration which lies between the full trans- and the intermediate ( $\mu_{\text{exp}} = 1.30$  D,  $\mu_{\text{calcd.}}^{\text{int}} = 0.65$  D). It is analogous to the configuration of tetraphenyl-

hydrazine in the conditions of combination. The methoxy groups, because of steric factors, are prevented from combination, and so the value of the half-wave potential of these compounds is almost the same ( $E_1$  of tetraphenylhydrazine = 0.61;  $E_1$  of tetra-*p*-anisylhydrazine = - 0.62) while in the corresponding disubstituted compound (IV, X = OCH<sub>3</sub>) the methoxy group clearly shows its electron-donor action and makes the reduction on the dropping mercury electrode much more difficult.

Thus, our results show that among the reasons for the contradictory effects of the same substituent on the tendency to dissociation into free radicals in a series of tetraaryl-substituted hydrazines (II) as compared to hexaaryl-substituted ethanes (I) the spatial factors have great importance.

On the basis of generalizations from the experimental data on the physicochemical properties of these substances and from the literature accounts of the chemical characteristics of the radicals of a series of diphenyl nitrogens we can express the opinion that the earlier conclusions of the contradictory effect of the substituents on the stability of the free radicals in the triphenylmethyl and diphenyl nitrogen series are not decisive, since they do not consider the significance of spatial factors.

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\*Original Russian pagination. See C. B. Translation.

# OBTAINING VARIOUSLY SUBSTITUTED TRIACIDOTRIAMINES OF TETRAVALENT PLATINUM

L. N. Essen

(Presented by Academician V. I. Splitsyn, July 8, 1958)

In our previous papers [1-4] we described methods of synthesis of five isomers (out of the fifteen theoretically possible) with the composition  $[\text{PyNH}_2\text{ClBrINO}_2\text{Pt}]$ .

Working out methods for obtaining the other isomers of this composition was not of major interest, though they could give many new interesting data on the reciprocal effects of atoms in complex molecules.

At the present time there is great interest in establishing the presence of optical isomers for compounds of this type. However, the resolution into optical antipodes of complex nonelectrolytes (and all the compounds of this type which we obtained earlier were nonelectrolytes) encounters great experimental difficulty. The method of adsorption on finely divided quartz which is suitable in this case has not found wide practical application. For this purpose it would be more suitable to synthesize the soluble differently substituted triacidotriamines of tetravalent platinum  $(a_1a_2a_3x_1x_2x_3\text{Pt})x$  and to attempt to resolve them by the usual method, the action of optically active acids.

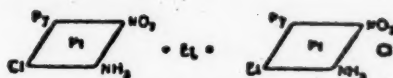
In this short communication are reported the results of experimental work on the synthesis of differently substituted triacidotriamines of tetravalent platinum.

The preparation of these compounds was carried out in three stages:

1) Obtaining differently substituted triamines of divalent platinum. 2) Transformation of these into triamines of tetravalent platinum. 3) Carrying out of substitution on the third coordinate. In carrying out this synthesis we took into consideration the literature data on getting asymmetric salts of divalent platinum of the Cleve type [5] and on getting methylamine and ethylamine compounds of platinum [6, 7].

We succeeded in synthesizing two differently substituted triacidotriamines of tetravalent platinum:  $[\text{PyNH}_2\text{EtNO}_2\text{ClBrPt}]\text{Cl}$  (Et = ethylamine,  $\text{C}_2\text{H}_5\text{NH}_2$ ) and  $[\text{PyNH}_2\text{MeNO}_2\text{BrClPt}]\text{Br}$  (Me = methylamine,  $\text{CH}_3\text{NH}_2$ ).

To obtain the first of these we began by obtaining the triamine of divalent platinum  $[\text{PyNH}_2\text{EtNO}_2\text{Pt}]\text{Cl}$  by the reaction:



For this purpose a sample of the salt  $[\text{PyNH}_2\text{ClNO}_2\text{Pt}]$  was heated in water with ethylamine until a colorless solution formed; ethylamine was added in small portions as a 50% solution. After evaporation of the solution there remained a colorless, slightly sticky, glassy mass, in which were long needle-shaped crystals. After treatment with ether this gave a white, crystalline powder.

Found %: Pt 45.78; 45.48; Cl 8.56;

$\text{H}_2\text{O}$  1.82

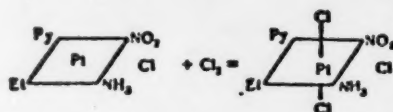
$[\text{PyNH}_2\text{EtNO}_2\text{Pt}]\text{Cl} \cdot \frac{1}{2} \text{H}_2\text{O}$  (molec. wt 426.8). Calculated %: Pt 45.74; Cl 8.32;

$\text{H}_2\text{O}$  2.11

• Translation of Russian - Publisher's note.

We obtained the triamine  $[\text{PyNH}_3\text{EtClPt}]\text{Cl}$  by a similar process.

As a starting substance for the synthesis of differently substituted triamines of tetravalent platinum we used the triamine which contained the nitro group,  $[\text{PyNH}_3\text{EtNO}_2\text{Pt}]\text{Cl}$ , since on the basis of our earlier studies it was known that the introduction of a nitro group into compounds of tetravalent platinum was especially difficult. The resulting triamine  $[\text{PyNH}_3\text{EtNO}_2\text{Pt}]\text{Cl}$  was oxidized with chlorine. The oxidation occurred according to the equation:



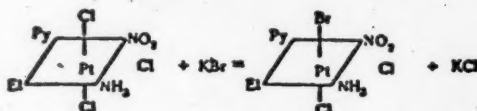
A change in the color of the solution occurred with the oxidation: from colorless it became yellow and sometimes showed a slight precipitate. When the solution was evaporated, it gave a yellow, crystalline substance. As analysis showed, this substance was the chloride  $[\text{PyNH}_3\text{EtNO}_2\text{Cl}_2\text{Pt}]\text{Cl}$  which contained water of crystallization, gradually lost on drying.

Analysis of the dry substance gave these results:

Found %: Pt 39,66; 40,32; 40,11;  
Cl 22,72; 22,54

$[\text{PyNH}_3\text{EtNO}_2\text{Cl}_2\text{Pt}]\text{Cl}$  (Molec. wt 488,8). Calculated %: Pt 39,94;  
Cl 22,04

The last stage in the synthesis was carried out by the reaction:



A sample of the salt  $[\text{PyNH}_3\text{EtNO}_2\text{Cl}_2\text{Pt}]\text{Cl}$  was dissolved in water and heated on a water bath for a half hour with potassium bromide, taken in stoichiometric amounts. The color of the solution gradually changed: from light yellow it became bright yellow. After the solution had been concentrated and cooled, a bright-yellow precipitate came down; it was separated from the mother liquor, washed several times with drops of cold water, and carefully dried.

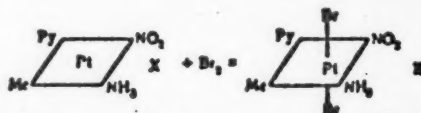
Found %: Pt 36,99; 37,10; EtCl + Br 27,99;  
28,57; Cl<sub>outer</sub> 7,03

$[\text{PyNH}_3\text{EtNO}_2\text{ClBrPt}]\text{Cl}$  (Molec. wt 533,2). Calculated %: Pt 36,62; EtCl + Br 28,31;  
Cl<sub>outer</sub> 6,65

The second differently substituted triacidotriamine of tetravalent platinum with the composition  $[\text{PyNH}_3\text{MeNO}_2\text{BrClPt}]\text{Br}$  was obtained as follows. To a weight of the diamine  $[\text{PyNH}_3\text{NO}_2\text{BrPt}]$  in hot water was added a 10% solution of methylamine in amounts required for the formation of a colorless solution. The solution was evaporated and from it a white, crystalline substance separated whose composition corresponded to the formula  $[\text{PyNH}_3\text{MeNO}_2\text{Pt}]\text{Br}$ .

By analogous methods from the diamines  $[\text{PyNH}_3(\text{NO}_2)_2\text{Pt}]$  and  $[\text{PyNH}_3\text{Br}_2\text{Pt}]$  we obtained the corresponding triamines  $[\text{PyNH}_3\text{MeNO}_2\text{Pt}]\text{NO}_2$  and  $[\text{PyNH}_3\text{MeBrPt}]\text{Br}$ .

As starting substances for further work we took the triamines  $[\text{PyNH}_3\text{MeNO}_2\text{Pt}]\text{Br}$  and  $[\text{PyNH}_3\text{MeNO}_2\text{Pt}]\text{NO}_2$ . Solutions of these salts were oxidized by bromine. The reaction went according to the equation:





The outer-sphere anion in the starting compounds had practically no effect on the composition of the oxidation product; since the solution contained a considerable concentration of bromine ions, crystallization from it gave the bromide  $(\text{PyNH}_3\text{MeNO}_2\text{Br}_2\text{Pt})\text{Br}$ . Its composition was confirmed by analysis.

Found %: Pt 32,67; 32,61; 32,90;  $\text{Br}_{\text{total}}$  39,11;

$\text{Br}_{\text{outer}}$  13,45.

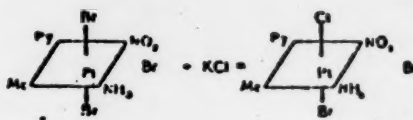
$[\text{PyNH}_3\text{MeNO}_2\text{Br}_2\text{Pt}]\text{Br}$  (Molec. wt 607,9). Calculated %: Pt 32,11

$\text{Br}_{\text{total}}$  39,43;

$\text{Br}_{\text{outer}}$  13,14.

The last stage consisted in replacement of one of the bromines in this compound on the  $\text{Br-Pt-Br}$  coordinate by chlorine.

Based on the facts obtained earlier, we expected that because of the great coordination firmness of bromine it would be harder to carry out this reaction than the above-described replacement of the chlorine on the  $\text{Cl-Pt-Cl}$  coordinate. Actually, this was so. In order to obtain the needed triacidotriamine by the equation



it was necessary to take more than the stoichiometric amount of potassium chloride and to carry out the reaction at higher temperature. As a result of the reaction we obtained a bright-yellow, crystalline substance.

Found %: Pt 34,57; 34,44;  $\text{Cl} + \text{Br}$  34,55;

34,27;  $\text{Br}_{\text{outer}}$  14,73

$[\text{PyNH}_3\text{MeNO}_2\text{BrClPt}]\text{Br}$  (Molec. wt 563,5). Calculated %: Pt 34,64;

$\text{Cl} + \text{Br}$  34,66;

$\text{Br}_{\text{outer}}$  14,18

The preparation of the triamines  $(\text{PyNH}_3\text{EtNO}_2\text{ClBrPt})\text{Cl}$  and  $(\text{PyNH}_3\text{MeNO}_2\text{BrClPt})\text{Br}$  offers the possibility of testing the coordination theory of resolution of differently substituted compounds of tetravalent platinum into optical antipodes.

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# THE STRUCTURE OF THE PRODUCTS OF ADDITION OF AROMATIC AMINES TO ZINC HALIDES

A. V. Ablov and T. I. Malinovskii

(Presented by Academician I. I. Cherniaev, June 26, 1958)

There are two closely connected theories which attempt to explain the effect produced by ligands on the behavior of d-electrons of the central atom in elements occupying the middle of the first long period of the Mendeleev system.

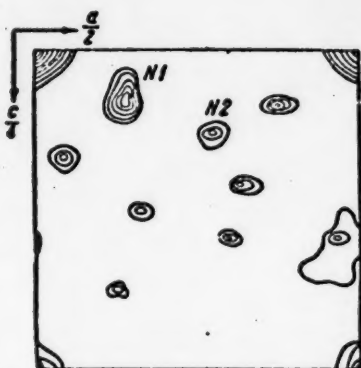


Fig. 1. Projection of function of inter-atomic vectors of  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  on plane (010). No. 1 - peak corresponding to vector Zn-Cl, No. 2 - peak corresponding to vector Cl-Cl

The first, also called the crystal-field theory, starts from the assumption that in the complexes the bond between the central atom and the ligand (ions and polar molecules) is electrostatic. It follows from the reasoning that the potential energy of the electrons in the degenerate d-state is changed in the electrical field of the ligand. In recent times this theory has been used for an explanation of the absorption spectra and stability of many complex ions.

Williams [1] considers that this theory in its present form does not correspond to the actual assumptions of the strength of the electrostatic fields formed by different ligands. A. V. Ablov and M. P. Filippov [2, 3] showed that the first absorption band in a complex of trivalent cobalt of the type  $[\text{Co en}_2 (\text{Amine}) \text{Halogen}]X_2$  did not depend on the dipole moment of the aromatic amine which contradicts the electrostatic theory of absorption spectra of complex compounds developed by Hartmann [4, 5] on the basis of the theory of the crystal field.

The second theory assumes that the bond in the complex has a partly covalent character. For the application of this theory it is possible to use the valence-bond method or the method of molecular orbitals. Van Vleck [6] considered binding and loosening states between combinations of  $\sigma$ -orbital of the ligand and  $d_{\gamma}$ -orbital of the cation. Griffiths and Owen [7] took into account, in addition, the  $\pi$ -orbital for the case in which the cation is an acceptor. Detailed consideration of this question showed that with an increased number of unsaturated ligands in the complex, its stability should rise. Williams [1] considers that binding of the  $\pi d_{\gamma}$  state can have a decisive effect on the form of the molecule, even in elements with a filled d-shell. For this reason the complex compounds of zinc with aromatic amines should have an octahedral structure.

These conclusions are not confirmed in compounds of divalent cobalt. Actually, while cobalt chloride dihydrate  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  [8] and the violet form of cobalt chloride dipyridinate  $\text{CoCl}_2 \cdot 2\text{Py}$  [9] have a chain structure with the coordination number for cobalt of 6, the product of addition of p-toluidine to cobalt chloride,  $\text{CoCl}_2 \cdot 2p\text{-H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , has a molecular lattice. In the molecule around the cobalt atom are arranged two atoms of chlorine and two atoms of nitrogen [10, 11].

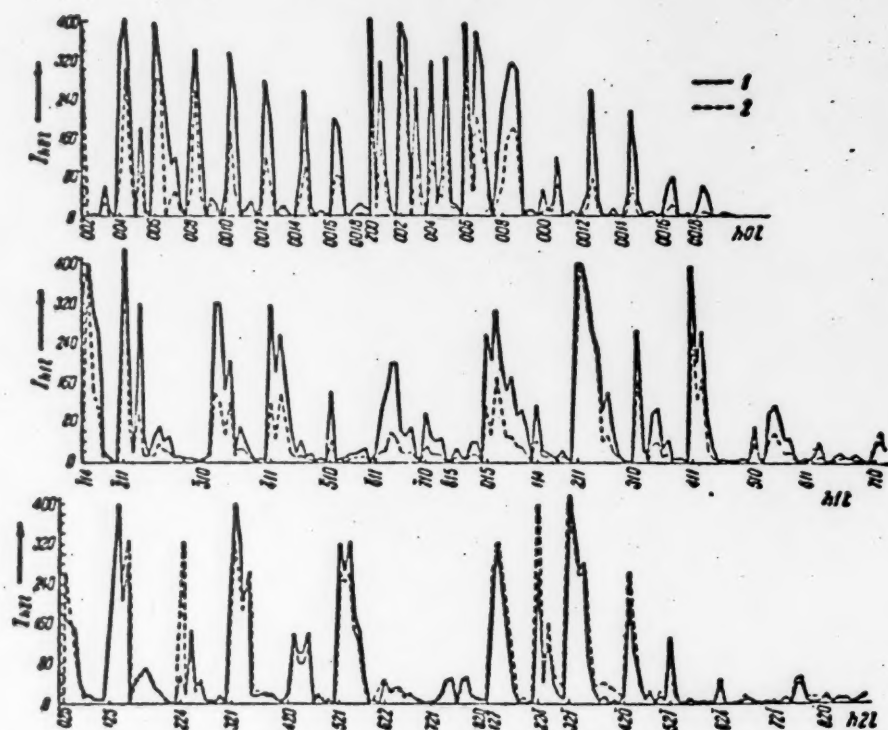


Fig. 2. Graphic comparison of intensities (I) of reflection of  $\text{ZnCl}_2 \cdot 2\text{p-toluidine}$  (1) and  $\text{CoCl}_2 \cdot 2\text{p-toluidine}$ .

It is known that the diammonate of zinc chloride and correspondingly, of zinc bromide, have a molecular crystal lattice where each zinc atom is surrounded by two atoms of halogen and two molecules of ammonia in an apex-distorted tetrahedron [12]. In a molecule of dichlorodiamino zinc the Zn-Cl and Zn-N bonds are covalent with lengths  $2.30 \pm 0.06$  and  $2.0 \pm 0.1$  Å respectively.

It is particularly interesting to explain the structure of the addition products of aromatic amines and zinc salts. For this purpose we studied the structure of the addition product of p-toluidine and zinc chloride  $\text{ZnCl}_2 \cdot 2\text{p-H}_2\text{NC}_6\text{H}_4\text{CH}_3$ . This compound was obtained by mixing slightly warmed solutions of anhydrous zinc chloride and p-toluidine in absolute ethyl alcohol. When the solution was cooled, colorless needle-like plates separated; they were washed with alcohol and dried to constant weight in a desiccator over calcium chloride.

Found %: Zn 18.63; Cl 20.18

$\text{ZnCl}_2 \cdot 2\text{C}_6\text{H}_5\text{N}$ . Calculated %: Zn 18.65; Cl 20.23

X-ray structure study of these crystals was carried out in the usual way. The parameters of the monoclinic cell, determined in an oscillation chamber, were:  $a = 12.44 \pm 0.05$  Å,  $b = 4.78 \pm 0.02$  Å,  $c = 26.2 \pm 0.1$  Å,  $\beta = 93^\circ 30' \pm 30'$ . The density, determined by a pycnometer, was 1.52 which gives for the number of formula units in the elementary cell  $n = 4.06 \approx 4$ . The density determined roentgenographically was 1.49. As a result of the indications of the X-ray plate we have established the following regularities of extinctions

Type of reflection

Conditions under which this type of reflection occurs

hkl  
h0l  
0k0

$h+k+l=2n$   
 $h=2n; l=2n$   
 $h=2n$

These regularities correspond to space groups  $I^h$ ,  $a = C_{2h}^2$  and  $I_a = C_2^2$ .

Further study was carried out with X-ray plates obtained in a chamber for photographing the reciprocal lattice with Mo-K $\alpha$  illumination. The total number of reflections used with the development of h0l, h1l and h2l was 421. The intensity was estimated visually, by the type of darkening. The value of  $F^2$  was found from calculation of the kinematic and polarization factors. On the basis of these data we constructed the two-dimensional  $F^2_{hk}$  series for the zero, first, and second layer lines

$$P_K(x, z) = \sum_{h=0}^K \sum_{k=0}^K F^2_{hk} \cdot \cos 2\pi (hx/a + lz/c)$$

( $K = 0, 1, 2$ ). On the projection the maxima 1 and 2 are clearly shown (Fig. 1); they were identified with the vectors Zn-Cl and Cl-Cl. From an analysis of the two dimensional  $F^2_{hk}$  series at the first and second layer lines  $P_1(xz)$  and  $P_2(xz)$ , we established that the vector Cl-Cl was parallel to the plane XOZ from which it follows that the chlorine atoms are connected with an axis of the second order, passing through the zinc atom. From a comparison of the height of the peaks on the projection of the first and second layer lines ( $P_1(xz)$  and  $P_2(xz)$ ) it was established that the chlorine atom is found at a height  $y/b = 0.3$  relative to the plane in which the zinc atom occurs. The Zn-Cl distance is  $2.35 \pm 0.05$  Å. This value cannot pretend to great accuracy in view of the method of projection of interatomic vectors used.

The observed distance indicates preferably a covalent bond of the central atom with the halogen, the same as in the structure of  $\text{CoCl}_2 \cdot 2p\text{-toluidine}$  [11]. The similarity of the lattice parameters, agreement of space group symmetry and also the similar diagrams of interatomic vectors establish the assumption of the same structure for the products of addition of *p*-toluidine to zinc chloride and cobalt chloride. We constructed a graphic comparison of the intensities of cobalt chloride di-*p*-toluidine and zinc chloride di-*p*-toluidine. As Fig. 2 shows, the intensities of both compounds have the same character of change from reflection to reflection, which confirms the same structure for these compounds.

Hence it follows that the structure of  $\text{Cl}_2 \cdot 2p\text{-toluidine}$  is molecular. The zinc atom is in the center of an almost regular tetrahedron, two apices of which are occupied by atoms of Cl and two by atoms of N.

Thus replacement of ammonia by aromatic amines does not change the coordination number of zinc in compounds of the type  $\text{ZnCl}_2 \cdot 2A$ , since this was found in the corresponding compounds of divalent cobalt.

The authors wish to express their thanks to Corresponding Member of the Academy of Sciences Ia. K. Syrkin for his discussion of the results.

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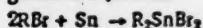
**STUDIES IN THE FIELD OF THE RADIATION CHEMISTRY OF  
ORGANOMETALLIC COMPOUNDS. GAMMA-RADIATION IN THE REACTION  
BETWEEN METALLIC TIN AND ALKYL HALIDES**

L. V. Abramova, N. I. Sheverdina, and Corresponding Member K. A. Kocheshkov

In the field of radiation chemistry there have been a number of studies of reactions under the influence of high-intensity radiation on water and aqueous solutions. Less attention has been paid to the reactions of organic compounds and to nonaqueous media. As far as we know, there have been no studies of process in metallorganic chemistry under the influence of such radiation.

In the systematic study of this question in various directions, we have investigated the reactions of alkyl and aryl halides with different metals, and, as one example, the reaction of alkyl halides with metallic tin, a reaction which is interesting from both the theoretical and the practical aspects\*.

These reactions can be shown by the general equation

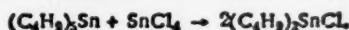


and probably occur by a more complex mechanism (see below); they do not take place at ordinary temperature. It requires a relatively high temperature for them to occur ( $200^\circ$  [1],  $300-350^\circ$  [2])\*\*.

Because of the severe reaction conditions, the final product is contaminated with considerable amounts (up to 25%) of  $R_2SnX$ , etc. While sealed vessels must be used here, strong explosions may occur [1] because of the accumulation of gaseous products.

Also, as Van der Kerk and Luijten showed [5], this reaction is limited to the lower alkyls (methyl, ethyl). When n-butyl bromide and tin are heated to  $180^\circ$  for several hours, the substances do not react: vapors of n-butyl bromide passed through molten tin give the same negative result; finally, as distinct from the preparation of methyl silicon or methyl germanium compounds [2], passage of the vapors of n-butyl chloride over a copper-tin alloy at  $300^\circ$  leads only to the formation of butene, tin chloride, and other nonmetalloorganic compounds.

Therefore the organic salts of di-n-butyl tin, such as the maleate or the laurate, which have the greatest effect in stabilizing vinyl chloride plastics, were obtained by these authors by a roundabout method, by disproportionation of tetraalkyl tin compounds by the method of Kocheshkov [6].



Although the yields here were nearly quantitative, it was first necessary to obtain tetrabutyl tin.

Hence, it is interesting to find a new path for direct preparation of the alkyl tin dihalide which would permit formation at ordinary pressures and temperatures and would use a new source of energy.

Therefore we set up the problem of studying the reaction of alkyl halides with metallic tin when they are irradiated with  $\gamma$ -rays. As the data given below show, the reaction between alkyl bromides and tin occurs at ordinary temperature and reaches a yield of 55 moles per 100 e.v. (based on the alkyl halide).

\* Tin organic compounds of the type  $R_2SnX_2$  have been described in the literature as stabilizers for vinyl chloride plastics [3] and also as catalysts in obtaining polyesters [4].

\*\* Only with the alkyl iodides, which are of little practical importance, can there be a reaction in sunlight (Cahours, 1860) (with partial decomposition at the same time and formation of iodine).

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original color without turning brown, forming tars, or fuming (hydrogen bromide). It had a weak odor of  $R_3SnX$  (which, as is known, is a very considerable contaminant in the thermal process). The tin, which had agglomerated into a dense mass, was washed several times with low boiling ( $\sim 40^\circ$ ) petroleum ether and the petroleum ether washings were added to the main filtrate. After the ether and unreacted butyl bromide had distilled off, the liquid di-n-butyltin dibromide remained. It was identified by transformation with ammonia into the oxide, and then by hydrochloric acid into the corresponding dichloride, b. p.  $40^\circ$  [5]; according to the literature di-n-butyltin dichloride has b. p.  $40.5^\circ$ . The yield (calculated on the bromide taken) reached 55 mole per 100 ev.

Reaction of tin with n-propyl bromide or ethyl bromide under  $\gamma$ -ray irradiation. Using analogous ratios of reagents and reaction conditions, we irradiated mixtures of n-propyl bromide and powdered tin and formed di-n-propyltin dibromide. After the usual treatment of distillation of petroleum ether and unreacted bromide, and cooling, we obtained a crystalline substance which, after recrystallization from n-hexane, melted at  $48^\circ$ ; according to the literature,  $49^\circ$  [8].

As in the previous experiment, the reaction mixture after irradiation had almost no contamination with tri-n-propyltin bromide, did not fume, and showed no signs of tarring. Yields are in Table 1.

When a mixture of 4 cc of ethyl bromide and 33 g of tin was irradiated as described above and treated in the usual way, it gave diethyltin dibromide with a yield of 38 mole per 100 ev (integral dose  $50 \cdot 10^6$  g). After the usual treatment we obtained 4.4 g of diethyltin dibromide with m. p.  $63^\circ$ ; according to the literature,  $64^\circ$  [1].

It was also of some interest to study the relation of the dibromides which were obtained to irradiation. A small amount of pure diethyltin dibromide or di-n-propyltin dibromide was irradiated with  $\gamma$ -rays. At integral doses of  $30 \cdot 10^6$  g no noticeable decomposition occurred. The melting point remained unchanged.

Ultraviolet illumination of a mixture of ethyl bromide and tin. A mixture of ethyl bromide (or n-propyl bromide) with excess tin powder was irradiated in a quartz ampule for 50 hours at  $50^\circ$  by a quartz lamp at a distance of about 20 cm from the source. After the usual treatment we could not find any organotin compound.

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# CIS-TRANS ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF ALUMINUM ORGANIC COMPOUNDS AND TITANIUM TETRACHLORIDE

Corresponding Member B. A. Dolgoplosk, E. N. Kropacheva, and K. V. Nel'son

As is known, the Ziegler catalyst in recent years has become very valuable for the synthesis of polymers with regular structures, especially cis-poly-isoprene [1-4]. Destruction of the structure of the chain by formation of trans-links has been connected up to now only with the effects of the physical and chemical characteristics of the catalyst on the nature of the combinations of the monomer (diene) during polymerization. In the present work it is shown that destruction of the regular character of the structure can be caused by isomerization of the cis-bonds in the already formed chain into trans-bonds under the influence of substances which are used to stimulate polymerization. Attempts to isomerize natural rubber into gutta percha under the influence of ultraviolet light or iodine [5] did not produce the desired effect. Ferri [7] first showed that under the influence of zinc chloride and titanium tetrachloride natural rubber undergoes changes which, according to the results of X-ray analysis, are accompanied by disappearance of the crystallization effect when the resin is stretched.

On the basis of these results the author concludes that under the influence of such agents there is isomerization of the cis-bonds of the natural rubber polymer chain into trans-bonds.

TABLE 1

Isomerization of Natural Rubber under the Influence of  $TiCl_4$  and Aluminum Organic Compounds at 90° and a Rubber Concentration of 2%.

Sample No.	Isomerizing agent	Content of isomerizing agent, wt. % of rubber	Duration of reaction, hours	Unsaturation, % of theory	Structure by infrared spectrum, %			
					Cis-1,4	Trans-1,4	3,4	1,2
1	—	—	—	99; 99.5	95	3	2	0
2	$TiCl_4$	10	10	86.5; 87	65	33	2	0
3	$TiCl_4$	10	10	84; 85	67	32	1	0
4	$TiCl_4$	10	10	Not determined	68	29	2	1
5	$TiCl_4$	50	10	61.5; 65.1	13	78	6	3
6	$TiCl_4$	10	1	75.4; 72.8	74	21	4	1
7	$TiCl_4$	10	20	68.5; 64.5	44	51	4	1
8	$AlEt_2Cl$	10	10	65; 65.5	58	40	2	0
9	$AlEt_3$	10	10	89; 85.4	49	47	2	2
	$AlEt_3$	10	10	83; 81	69	30	1	0
10	Ethyl di-(2phenyl-butyl)aluminum	10	10	70; 74	43	54	2	1
11	Triisobutylaluminum	10	10					

The first isomerization of a cis-1,4-bond into a trans-bond in polybutadiene under the influence of ultraviolet light in the presence of organic compounds of bromine or sulfur was carried out and described by Colub [7]. In natural rubber the analogous formation of trans-bonds under these conditions was not found.

A study of the isomerizing effect of  $TiCl_4$  and aluminum organic compounds was carried out by us on so-

lutions of milled natural rubber (NR) in benzene in sealed glass ampules. The benzene was dried before use and distilled over sodium. All the work was carried out in an atmosphere of dry argon. For each sample we determined the unsaturation and the microstructure of the chain.

The study of the microstructure of the polyisoprene was carried out by infrared spectra; the relative content of the different bond configurations of the polymer chain was determined by absorption in the region 800-1000  $\text{cm}^{-1}$ . We used the method worked out earlier by one of us [8]. The results of the quantitative investigation of the microstructure of the initial NR samples and the samples submitted to the action of isomerizing agents are given in Table 1, where we show the content of cis-1,4; trans-1,4; 1,2; and 3,4 configurations calculated on the concentration of links with the double bond  $\text{C}=\text{C}$ .

It follows from these data that the components of the Ziegler catalyst used for carrying out the polymerization ( $\text{TiCl}_4$ ,  $\text{AlR}_3$ ,  $\text{AlR}_2\text{Cl}$ ) have an isomerizing effect on the polymer chain of natural rubber.

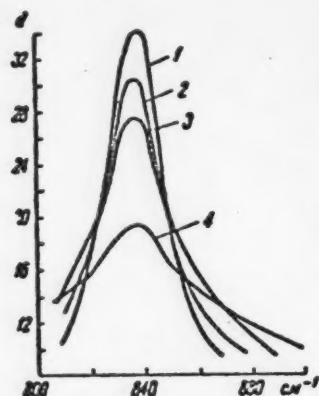


Fig. 1. Infrared absorption bands at different content in the polymer chain of cis-trans configurations. 1 - natural rubber (NR): cis 95%, trans 5%; 2 - isomerized NR, cis 65%, trans 35%; 3 - isomerized NR, cis 44%, trans 51%; 4 - isomerized NR, cis 13%, trans 78%.

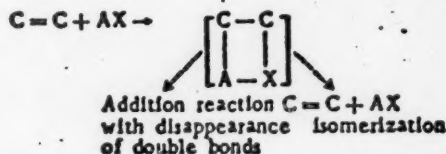
In the example with titanium tetrachloride it was shown that the number of trans-links increased with increasing concentration of isomerizing agent and duration of the reaction.

The effect of isomerization of polyisoprene which we observed is clearly illustrated by the curves of Fig. 1 where we give the infrared absorption bands which correspond to different contents of cis and trans-links.

Since the molar absorption coefficient  $K$  for the cis-links at  $\nu = 839 \text{ cm}^{-1}$  is 52 and for the trans-links at the same point in the spectrum it is 23, then the relative decrease in intensity of the absorption bands, which depends on the cis-trans-configuration with the same concentration of links of the double bond  $\text{C}=\text{C}$ , at once characterizes the decrease in content of cis-links in the polymer chain and the corresponding increase in trans-links.

The isomerization processes which occur under the influence of these agents are accompanied by a decrease in the unsaturation of the polymer. The considerable decrease in unsaturation while the polymer keeps its solubility evidently depends on a process of cyclization in the chain, as was observed in one of our investigations.

The decrease in unsaturation is connected with the ability of the above-mentioned compounds to combine with the  $\text{C}=\text{C}$  bond. This is evidently preceded by the formation of an unstable complex which can split with regeneration of the starting substance. Isomerization can proceed in this intermediate stage:



We have established that in the case of ethyl aluminum dichloride the natural rubber undergoes a deeper, secondary change: the process goes to the formation of an insoluble, high melting, amorphous powder. An analogous effect is found when a greater quantity of  $\text{TiCl}_4$  is used (100 wt. % of the rubber).

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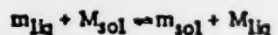
# DETERMINATION OF COMPOSITION AND STABILITY CONSTANT OF COMPLEX LEAD CHLORIDES FROM EXPERIMENTS ON THE DISTRIBUTION OF THE RADIOACTIVE ISOTOPE BETWEEN PRECIPITATE AND SOLUTION

K. B. Zaborenko, I. V. Kolosov, and V. V. Fomin

(Presented by Academician V. I. Spitsyn, July 12, 1958)

V. G. Khlopin and his school have shown [1] that in the distribution of microelements between precipitate and solution of isomorphous compounds of the macroelements it is possible to attain a true thermodynamic equilibrium.

We will consider co-crystallization as a reversible reaction of exchange of ions with the same valence:



The equilibrium constant of this reaction is

$$K = \frac{[m]_{sol} [M]_{liq}}{[m]_{liq} [M]_{sol}} \quad (1)$$

In this equation,  $m$  is the microelement,  $M$  the macroelement. The subscript shows the phase (solid and liquid) in which the ions occur; the square brackets give their activities. However, if the concentration of the microelement in the solid phase is small and the ionic strength of the solution is kept constant, then the total activity coefficient has a practically constant value. Therefore, in place of the activity we can take the concentration, including the whole activity coefficient in the equilibrium constant. Equation (1) is also applicable to the case of distribution of isomorphous ions of the microcomponent between the surface and the solution (primary ion-exchange adsorption).

V. G. Khlopin showed [1] that the presence in the water solution of ions which form complexes with one of the elements  $m$  or  $M$  causes a change in the "distribution" constants. In the remainder of this paper we will call the distribution constant the value which is obtained by calculation according to formula (1) where instead of the equilibrium concentration are put the concentrations determined by experimental analysis.

The change in distribution coefficient depending on concentration of complex-forming ion is shown when ion complexes occur in solution. An example of such an effect is given in the work of V. G. Khlopin and A. P. Ratner [2], and of Kading [3]. In the latter case it can be shown that the change in  $D$  is determined basically by the change in activity.

We have worked out a method of calculation for determining the composition and stability constant for complex ions. We have studied the distribution in the system  $SrSO_4$ - $Pb^{212}$ - $SO_4$ - $HCl$ . The experiments were carried out by well-known methods developed by V. G. Khlopin and his students [1, 4, 5]. If the experimental data are expressed by the formula

$$D = \frac{x(1-y)}{y(1-x)} \quad (2)$$

(where  $x$  and  $y$  are the amounts of micro and macrocomponents in the precipitate,  $1-x$  and  $1-y$ , the corresponding amounts in the solution) then in the absence of complex formation,  $D_0 = K$ ; in the presence of complex formation, if the analytical concentrations are used in formula (2), then the distribution coefficient is a function of the concentration of the complex-forming ion. The calculation is considerably simplified if the macrocomponent



TABLE 1

HCl concentration*, mole/liter	SrSO <sub>4</sub> solubility, g/liter	D°	$\frac{D' - 1}{D'}$ [Cl']
0	1.94	0.39	
0.01	1.93	0.23	63
0.05	1.90	0.11	52
0.10	1.86	0.09	31
0.20	1.81	0.09	17
0.40	1.75	0.09	8
0.50	1.74	0.08	8
1.00	2.00	0.08	4

\*Ionic strength of solution  $\mu = 1$ .

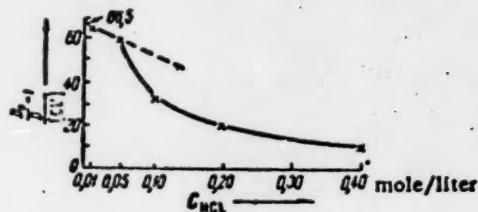


Fig. 1

does not form a stable complex compound with ions of the complex former, and also basic or acid salts and complex ions do not enter the lattice of the macrocomponent compound. When equilibrium is reached in our system:  $Pb^{++}_{liq} + SrSO_{4sol} \rightleftharpoons PbSO_{4sol} + Sr^{++}_{liq}$

$$D_0 = \frac{[PbSO_{4sol}][Sr^{++}_{liq}]}{[Pb^{++}_{liq}][SrSO_{4sol}]} \quad (3)$$

It was shown that strontium ions do not form stable complex compounds with chloride ions. In the presence of chloride ions which form complexes of the type  $[PbCl_j]^{2-j}$ , the distribution coefficient  $D$  will differ from the equilibrium constant  $D_0$ , since instead of the concentration of the ion  $[Pb^{++}]_{liq}$  which should be in equation (3) there will be the analytical concentration, equal in this case to  $C_{Pb} = [Pb^{++}](1 + \sum \beta_j [Cl^-]^j)$ , where  $\beta_j$  is the stability constant of the corresponding complex ion  $PbCl_j^{2-j}$

$$\beta_j = \frac{[PbCl_j]^{2-j}}{[Pb^{++}][Cl^-]^j} \quad (4)$$

Therefore the distribution coefficient

$$D = \frac{[PbSO_{4sol}][Sr^{++}_{liq}]}{[SrSO_{4sol}][Pb]_{liq}} = \frac{[PbSO_{4sol}][Sr^{++}_{liq}]}{[SrSO_{4sol}][Pb^{++}]_{liq}(1 + \sum \beta_j [Cl^-]^j)} = \frac{D_0}{1 + \sum \beta_j [Cl^-]^j} \quad (4a)$$

or

$$\frac{D_0}{D} - 1 = \sum \beta_j [Cl^-]^j \quad (5)$$

It is clear that the basic equation (5) for calculating the composition and stability constant of the complex compound by use of the distribution law is analogous to the known equation for ion exchange and extraction. For determination of  $\beta_j$  and  $\beta_j$  it is necessary to obtain the relation of  $D$  to the concentration of complex-forming substance at constant ion strength of the solution. The treatment of the resulting data can be carried out by any of the known methods [6-9].

## EXPERIMENTAL

First we determined the solubility of strontium sulfate labeled with  $Sr^{88}$  in solutions which contained HCl and HClO<sub>4</sub> at different ratios with ionic strength equal to one. As kinetic experiments showed equilibrium "from below" was established sufficiently rapidly, in 30-40 min (at a rate of stirring of 1300 r. p. m.) We did not succeed in establishing the solubility "from above" since we obtained a very supersaturated solution and the supersaturation was not eliminated for several days. Therefore, for a solution of the basic problem, we studied the distribution of  $Pb^{222}$  between the surface of the precipitate and the saturated solution of given composition.

When we used equations (2) and (3) for the primary exchange adsorption, the concentration of  $(SrSO_4)_{sol}$  was proportional to the weight of precipitate, which was correct when we used a repeatedly recrystallized suspension.  $[SrSO_4]_{sol} = ky$ ; the proportionality coefficient  $k$  can be combined with the constant  $D_0$  then  $Dk = D^0$ .

All the experimental data given in Table 1 were obtained as averages of 4-7 determinations. The mean square error for the solubility values and  $D^*$  did not exceed 4.5 and 10%. From the data of the last column we constructed the relation of

$$\frac{D^*}{D} - 1$$

$$\frac{[Cl^-]}{[Cl^-]}$$

to the concentration of  $[Cl^-]$ .

According to equation (5) this function should be increasing. Analysis of the resulting curve showed the presence of a side process as a result of which the value of  $D^*$  fell more slowly than would follow from equation (5). This can be explained by secondary adsorption of the negatively charged lead ions of the suspension, contaminated in the acid solution by positively charged ones. This was confirmed by special adsorption experiments. However, in the field of small  $[Cl^-]$  concentrations where adsorption of the negatively charged complex ions can be neglected, it becomes possible to calculate the primary constants. Extrapolation of the curve (Fig. 1) to its intersection with the ordinate gave  $\beta_1 = 65 \pm 9$ ; the resulting value does not differ from that given in the literature [10].

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# A CHEMICAL METHOD FOR HOMOGENIZATION OF CELLULOSE ACCORDING TO MOLECULAR WEIGHT

V. I. Ivanov, B. A. Zakharov, G. A. Krylova, and N. G. V'lunova

(Presented by Academician V. A. Kargin, July 11, 1958)

In a previous communication [1] we confirmed experimentally our theoretical assumption of the close connection between strength of cellulose samples and homogeneity in chain length of the cellulose. Calculations of viscosity showed [2] that homogeneity was also important in the viscosity behavior of concentrated cellulose solutions. In this connection it became interesting to evaluate different chemical processes used in the treatment of cellulose from the point of view of homogenization. From the literature data we can conclude that present day processes of digesting [3], air or chemical degradation [4, 5], bleaching [3] or hydrolysis with hydrochloric [6] or sulfuric acids do not give effective homogenization of cellulose.

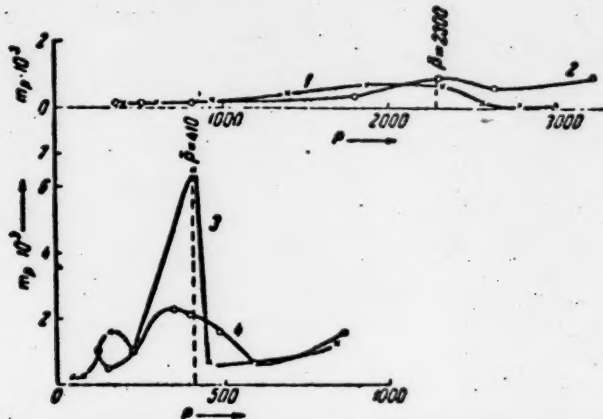


Fig. 1. Mass distribution function. 1 - Cotton cellulose according to Timell [11], 2 - Initial cotton cellulose prepared according to Corey and Gray, 3 - cotton cellulose treated with dilute nitric acid, 4 - cotton cellulose treated with dilute hydrochloric acid.

Experiments on the absorption by cellulose of acids from water solution were carried out with cotton cellulose (prepared according to Corey and Gray) and wood cellulose (cellulose sulfate obtained by the method worked out in the Institute of Organic Chemistry, Academy of Sciences, USSR). Treatment with nitric acid was carried out at 92° with a concentration of 0.2 N for 1 hour for cotton cellulose and 30 min for wood cellulose. Cotton cellulose was treated under the same conditions with hydrochloric acid.

The homogenizing effect was judged by the mass distribution function calculated from the data of some improved standards [8] of fractionally precipitated cellulose trinitro esters. The degree of polymerization (P) was

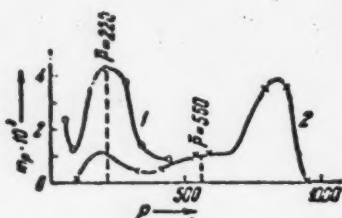


Fig. 2. Mass distribution function. 1 - Wood cellulose treated with dilute nitric acid, 2 - starting wood cellulose sulfate, treated by the method of Inst. Org. Chem., Acad. Sci. USSR.

with a maximum on the mass distribution curve at  $P = 850$  (Fig. 2, 2). The action of nitric acid on this cellulose for 30 min also gives homogenization, but the maximum on the mass distribution curve is shifted greatly to the side of the low molecular-weight range and occurs at  $P = 220$ .

These results allow us to conclude that treatment of cellulose with dilute nitric acid can serve as a method of chemical homogenization of cellulose by chain length. A corresponding choice of conditions for combined chemical and physicochemical homogenization (concentration, temperature, duration) can give a high degree of homogenization at any desired degree of polymerization which corresponds to strength of the different types of cellulose (fibers, paper, film).

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\*Original Russian pagination. See C. B. Translation.



# THE CATALYTIC REACTION OF ALKYLDICHLOROSILANES WITH HALOGEN-SUBSTITUTED BENZENES

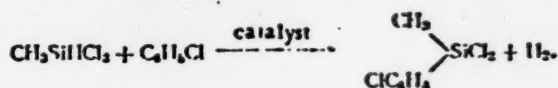
G. N. Mal'nova, E. P. Mikheev, A. I. Klehanskii, and N. P. Fillimonova

(Presented by Academician B. A. Kazanskii, July 14, 1958)

The reaction of alkyldichlorosilanes with halogen-substituted benzene has been very briefly mentioned in some patent literature. According to one patent [1], in an autoclave at 450° without a catalyst, methylphenyldichlorosilane is formed from methyldichlorosilane and chlorobenzene according to the equation:



The same substances react differently in the presence of  $\text{AlCl}_3$  or  $\text{BCl}_3$  [2]: in an autoclave at 150-300° occurs formation of methylchlorophenyldichlorosilane in about 6% yield from a charge of methyldichlorosilane according to the scheme:

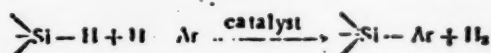


We have studied the catalytic reaction of methyldichlorosilane with chlorobenzene and fluorobenzene, and of ethyldichlorosilane with chlorobenzene.

In the present paper we have used boric acid as the catalyst, or, more correctly, as the substance from which the catalyst is formed; before the beginning of the main reaction it reacts with the alkyldichlorosilane with evolution of hydrogen chloride and formation of a compound which is soluble in the reaction mixture and which contains the bonds  $\text{Si}-\text{O}-\text{B}$



We were convinced by the study of the catalytic reaction of alkyldichlorosilanes with benzene [3] that the use of boric acid for arylation of the  $\text{Si-H}$  bond by the reaction



was more satisfactory than the use of other catalysts because of the great availability of boric acid, the convenience of its application, and the adequate catalytic activity of the product of its reaction with chlorosilanes.

The experiments on the catalytic reaction of alkyldichlorosilanes with halogen-substituted benzenes were carried out in a stainless steel autoclave with a capacity of 0.6 liters. The autoclave was filled to 50-60% of its volume with the starting mixture, to which boric acid was added. After the autoclave had been hermetically sealed it was placed in a heated oil bath. The temperature in the autoclave reached a constant value after 20-40 min. The reaction mixture was heated at this temperature until increase in pressure stopped, and then heated

TABLE 1

Synthesis Temp., (°C)	Yield $\begin{matrix} \text{C}_6\text{H}_5\text{SiCl}_2 \\ \text{C}_6\text{H}_4\text{SiCl}_2 \end{matrix}$ % of $\begin{matrix} \text{C}_6\text{H}_5\text{SiHCl}_2 \\ \text{C}_6\text{H}_4\text{SiHCl}_2 \end{matrix}$		% of used but unreacted	
	Used	Reacted	$\text{C}_6\text{H}_5\text{SiHCl}_2$	$\text{C}_6\text{H}_4\text{SiCl}_2$
260	18,6	24,8	24,8	80,8
270	17,1	21,2	19,6	76,8
285	16,3	18,7	12,8	75,0

TABLE 2

Starting aromatic compound	Minimum temperature for synthesis, °C	Optimum amount of boric acid, % of wt. of mixture	Yield of $\begin{matrix} \text{CH}_3\text{SiCl}_2 \\ \text{XC}_6\text{H}_4\text{SiCl}_2 \\ \text{CH}_3\text{SiHCl}_2 \end{matrix}$ % of
Benzene	240 ± 5	0,1	40
Chlorobenzene	250 ± 5	0,3	24
Fluorobenzene	255 ± 5	0,3	18

of methyldichlorosilane, 298.8 g of chlorobenzene, and 1.2 g of boric acid, or 111 g of ethyldichlorosilane, 287 g of chlorobenzene, and 1.19 g of boric acid. The temperature required to initiate the reaction of methyldichlorosilane with chlorobenzene was 255°. After 20 min from the start of the reaction it was permissible to lower the temperature by 5° without notable change in rate of the process. The temperature of the reaction of ethyldichlorosilane with chlorobenzene was 10° higher. These temperatures were optimal.

In Table 1 we give the relation of yield of ethylchlorophenyldichlorosilane to temperature of the synthesis.

When methyldichlorosilane reacted with chlorobenzene under the conditions described, we obtained a reaction mixture of the following composition: - 6% unchanged methyldichlorosilane, - 7% methyltrichlorosilane, - 5% dimethyldichlorosilane, - 60% unchanged chlorobenzene, - 4% of an intermediate fraction, with b. p. 44-128°/29 mm, - 10% methylchlorophenyldichlorosilane, and - 5% products in the still residue. The gaseous reaction products, formed in the amount of 0.32 g-mole per 1 g-mole of taken methyldichlorosilane consisted of 86.5-87.5% hydrogen, 9-10% methane, and 0.7-1% hydrogen chloride. When the reaction mixture was rectified, the fraction of methylchlorophenyldichlorosilane, a mixture of o-, m-, and p-isomers, had b. p. 232-238°;  $d_4^{20}$  1.2920 - 1.2965;  $n_D^{20}$  1.5338 - 1.5342;  $M_{rD}$  found 54.09-54.26, calculated 54.08

Found %: hydrolyzing Cl 31.21-31.97  
Calculated %: hydrolyzing Cl 31.43

The isomers were contained in the isolated fraction of methylchlorophenyldichlorosilane in the following ratio: ortho - 20%, meta - 45%, para - 35%\*. The yield of methylchlorophenyldichlorosilanes was 24% of the reacting methyldichlorosilane; in a larger autoclave the yield reached 27%.

In the reaction of ethyldichlorosilane with chlorobenzene under optimum conditions, we obtained a mixture which contained: - 7% unchanged ethyldichlorosilane, - 5% ethyltrichlorosilane, - 2% diethyldichlorosilane, - 60% chlorobenzene, - 4% intermediate fraction with b. p. 37.5-135.5°/18 mm, 9.6% ethylchlorophenyldichlorosilane, and about 6% of products which remained in the distilling flask. The gaseous reaction products, which formed in the amount of 0.32 g-mole per g-mole of ethyldichlorosilane put in the reaction, contained 90% hydrogen and 5% ethane. The fraction of the reaction mixture isolated by rectification and which contained the o-,

\*The ratio of isomers in the methylchlorophenyldichlorosilane fraction was determined by the method of combination light scattering by K. K. Popkov, for which we express thanks.

15-20 min longer. At the end of heating, the autoclave was removed from the bath and cooled to room temperature. The gaseous reaction products were collected in a gasometer and the liquid product was rectified on a column with the effectiveness of 14 theoretical plates. The low boiling fraction was distilled at atmospheric pressure, and rectification of the high boiling product of the reaction was carried out in a vacuum.

Because of the great thermal stability of the halobenzenes, they were used in excess, which had a favorable effect on the yield of alkylhalophenyldichlorosilanes. We took as the optimum molar ratio of alkylidichlorosilane to halobenzene, 1:3. A number of experiments showed that the addition of 0.3% of the weight of the reaction mass of boric acid was the optimum. A larger amount of boric acid greatly hastened the disproportionation of the alkylidichlorosilane; a smaller amount did not assure a fast enough reaction; in both cases the yield of alkylhalophenyldichlorosilane fell.

The reactions of methyl- and ethyldichlorosilane with chlorobenzene. In the autoclave we placed 101.2 g

m-, and p-isomers of ethylchlorophenyldichlorosilane had a b. p. 255-258°;  $d_4^{25}$  1.2592 - 1.2621;  $n_D^{25}$  1.5298 - 1.5317;  $MR_D$  found 58.76-58.83, calculated, 58.71.

Found %: hydrolyzing Cl 29.91-30.36

Calculated %: hydrolyzing Cl 29.59

The yield of ethylchlorophenyldichlorosilane reached 25% on the reacting ethyldichlorosilane.

Reaction of methyldichlorosilane with fluorobenzene. We placed in the autoclave 100 g of methyldichlorosilane, 250 g of fluorobenzene, and 1.05 g of boric acid. The minimum temperature required for starting the reaction was 255-260°; it was also the optimum. As a result of the reaction under the above conditions there was formed: a mixture of liquid substances which contained - 8% methylfluorophenyldichlorosilane, and gaseous products, in the amount of 0.35 mole per g-mole of methyldichlorosilane put into the reaction, which contained 83-86% hydrogen and 12-14% methane.

The liquid reaction product was separated by rectification to give a mixture of o-, m-, and p-methylfluorophenyldichlorosilanes with b. p. 196-199.7°;  $d_4^{20}$  1.2438 - 1.2492;  $n_D^{20}$  1.4960 - 1.4998;  $MR_D$  found 49.06-49.32, calculated 49.27.

Found %: Cl 33.66-34.20

Calculated %: Cl 33.91

The ratio of isomers in the isolated fraction of methylfluorophenyldichlorosilane was: ortho, - 25%, meta, - 60%, and para, - 15%. The yield of methylfluorophenyldichlorosilane was 18% of the reacting methyldichlorosilane.

The conditions for reaction of methyldichlorosilane with benzene and its halogen substituents, and also the yield of reaction products, are given in Table 2, and indicate that in this reaction there is a regular decrease in reactivity of the benzene ring when hydrogen is replaced in it by an atom of halogen. The tendency to reduced reactivity is stronger, the greater the polarity of the halogen.

Received July 10, 1958

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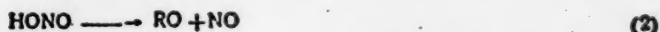
## THE REACTION OF ALKYL RADICALS WITH NITROGEN DIOXIDE

I. V. Patsevich, Academician A. V. Topchlev, and V. Ia. Shtern

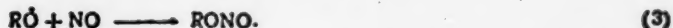
According to the present ideas of the main elementary process in gas phase nitration of alkanes there is reaction of the alkyl radical  $\dot{R}$  with  $\text{NO}_2$ . It is assumed that this occurs by two parallel paths, with formation of a nitrocompound and an alkyl nitrite



Further transformation of the alkyl nitrite is usually considered the source of the oxidation and destruction of the paraffin chain which actually occurs in the nitration product. It is assumed that the first event in the transformation of the alkyl nitrite is its decomposition according to the equation



Such a decomposition may occur thermally [1], or, as Gray assumes [2], at the moment when the alkyl nitrite is obtained by equation (1b). Gray explains this rapid decomposition by the fact that in the formation of the  $\text{R}'\text{CH}_2\text{-O-N-O}$  bond 57 kcal/mole of energy is evolved, and for breaking the  $\text{R}'\text{CH}_2\text{-O-NO}$  bond only 37 kcal/mole is required. The alkoxyl radical in its further transformations gives such oxidation products as aldehydes,  $\text{CO}$ ,  $\text{CO}_2$ . Also, by reacting with  $\text{NO}$  it can give a nitrite by secondary formation



These ideas of the mechanism of nitration are hypothetical and have never been tested directly by experiment. In the present work we have studied directly the reaction of  $\dot{R}$  with  $\text{NO}_2$  at low temperature, when thermal changes in intermediate and final products have been excluded. This is possible since  $\text{NO}_2$ , with an unpaired electron, is a molecule which resembles a radical and the reaction of  $\dot{R} + \text{NO}_2$  goes easily at low temperature. The purpose of the work was to show whether there were in fact the two pathways (1a) and (1b), to obtain data on the further behavior of  $\text{RONO}$ , and to determine from the relationship of amounts of  $\text{RNO}_2$  and  $\text{RONO}$  formed to temperature, the difference in energy of activation ( $\Delta E$ ) and the ratio of the steric factors  $f_1$  and  $f_2$  of these pathways

$$\frac{\Sigma \text{RNO}_2}{\Sigma \text{RONO}} = \frac{f_1}{f_2} e^{\Delta E/RT}$$

The alkyl radicals were obtained by reaction of hydrogen atoms with  $\text{C}_2\text{H}_4$ . A stream of molecular hydrogen which contained H atoms was passed from a discharge tube into the reactor, where two inlets admitted  $\text{C}_2\text{H}_4$  and  $\text{NO}_2$ . The distance from the point of introducing  $\text{C}_2\text{H}_4$  to the inlet for  $\text{NO}_2$  could be changed and thus the point where the radicals  $\dot{R}$  meet the  $\text{NO}_2$  along the tube could be changed.

In the products from the different series of reactions we determined:





TABLE 1

Composition of the Product of Reaction of  $\dot{R}$  with  $NO_2$  in the Presence of H Atoms,  $t = 20^\circ$  (mole percent).

$CH_4$	$C_2H_6$	$C_2H_4$	CO	$CO_2$	HCHO	RONO	$RNO_2$
19,1	5,2	59,0	9,0	1,2	5,15	0,94	0,7
22,2	5,65	55,5	6,3	1,24	7,1	1,0	0,85

TABLE 2

Behavior of  $CH_3NO_2$  under Conditions of Experiment without Excess Atoms of H.

Current strength in discharge tube, a	$CH_3NO_2$ found, mm	
	Without introduction of $CH_3NO_2$	With introduction of $CH_3NO_2$
0,00	0,0	0,0216
0,07	0,00966	0,0309

The hydrocarbon gases were analyzed chromatographically on carbon and silica gel columns;  $CO$ ,  $CO_2$ , and  $NO$  were determined by absorption in solutions of cuprous chloride, alkali, and hydrogen peroxide respectively. The determination of alkyl nitrite was carried out by the polarographic method which we worked out [3]. We also worked out a method for polarographic determination of nitroparaffins, alkyl nitrites, and aldehydes in each others presence.

At the start we made a preliminary study of the processes which can evidently proceed in the reactor along with the main reaction which we studied,  $\dot{R} + NO_2$ .

In the reaction of H atoms with  $C_2H_4$  we found only  $CH_4$  and  $C_2H_6$ . Heavier hydrocarbons which have been found in this case in a number of studies [4-6] in varying amounts depending on the experimental conditions were not found under our conditions ( $P_{H_2} = 2,3$  mm,  $P_{C_2H_4} = 0,05$  mm,  $I = 0,07-0,75$  a,  $t = 20-90^\circ$ ). Such a difference must be ascribed to the high concentration of H atoms in our experiments.

TABLE 3

Composition of the Product of Reaction of  $\dot{R}$  with  $NO_2$  without Excess H atoms

$t, ^\circ C$	Found, mole %		$\frac{RNO_2}{RONO}$	$t, ^\circ C$	Found mole %		$\frac{RNO_2}{RONO}$
	RONO	$RNO_2$			RONO	$RNO_2$	
96	31,8	68,2	2,14	-15	21,6	78,4	3,62
50	29,8	70,2	2,35	96	30,0	70,0	2,33
18	29,0	71,0	2,45	50	26,5	73,5	2,76
18	26,3	73,7	2,8	18	22,0	78,0	3,55
				-15	17,6	82,4	4,67

We also showed that in the reaction of H atoms with  $NO_2$  ( $P_{H_2} = 2,3$  mm,  $P_{NO_2} = 0,08$  mm,  $I = 0,75$  a,  $t = 20^\circ$ ),  $NO$  was formed. Finally, we showed that under our conditions low pressure and low temperature prevent reaction of  $C_2H_4$  with  $NO_2$ .

The first series of experiments in studying the reaction of  $\dot{R}$  with  $NO_2$  was carried out with  $C_2H_4$  and  $NO_2$  inlets at the same place in the reactor ( $P_{H_2} = 2,3$  mm,  $P_{C_2H_4} = 0,05$  mm,  $P_{NO_2} = 0,08$  mm,  $I = 0,75$  a,  $v_{stream} = 1$  m/sec). In this case the reaction  $\dot{R} + NO_2$  proceeds in the presence of excess H atoms. The results of two typical experiments of this series are given in Table 1.

As Table 1 shows,  $RNO_2$  and  $RONO$  were found in the products of the experiment, that is, there actually are two paths for the reaction of  $\dot{R}$  with  $NO_2$ . Since the thermal decomposition of  $RNO_2$  and  $RONO$  is excluded at room temperature, the formation of the oxidation products ( $CO$ ,  $CO_2$ , and  $HCHO$ ) can be considered as evidence of the correctness of the ideas of Gray on the splitting of  $RONO$  at the moment of its formation. In this case we can assume that as a result of the reaction of  $\dot{R}O$  radicals which are formed with H atoms and  $NO_2$ , aldehyde,  $CO$ , and  $CO_2$  are formed, and the presence of  $RONO$  in the product is explained by its secondary formation from the

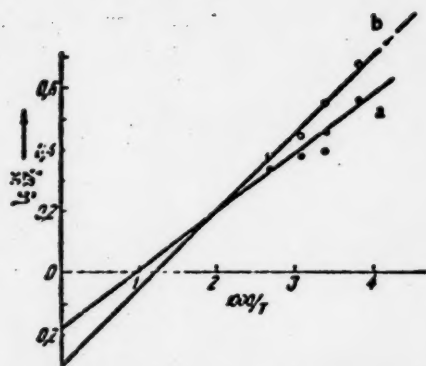


Fig. 1. Determination of the difference in energy of activation of the two paths of reaction of  $\dot{R}$  with  $\text{NO}_2$ . a - First series of experiments, b - second series of experiments.

TABLE 4

Difference in Energy of Activation and Ratio of Steric Factors of the Reaction of  $\dot{R}$  with  $\text{NO}_2$

$\Delta E$ , kcal/mole	$f_1/f_2$
0.84	0.66
1.21	0.50

TABLE 5

Effect of Surface on Reaction of  $\dot{R}$  with  $\text{NO}_2$

	Found, mole %		$\frac{\text{RNO}_2}{\text{RONO}}$
	$\text{RNO}_2$	$\text{RONO}$	
Without covering	78	22	3.5
KCl cover	76.5	23.5	3.3
$\text{K}_2\text{B}_4\text{O}_7$ cover	77.5	22.5	3.4

reaction which indicates the presence of thermal decomposition of  $\text{RONO}$  at this temperature). Thus the products of the reaction of  $\dot{R} + \text{NO}_2$  in this case are only  $\text{RNO}_2$  and  $\text{RONO}$ .

If we follow the Gray theory of the splitting of  $\text{RONO}$  at the moment of its formation in the reaction  $\dot{R} + \text{NO}_2$ , we must explain its presence in the products of the experiments described above. "Secondary" nitrite, in the opinion of Gray, is formed by equation (3). However, under the conditions of our experiment, only slight amounts of  $\text{NO}$  can be present in the reaction zone, along with a great excess of  $\text{NO}_2$ . Hence, as a result of the secondary reaction of  $\text{RO}$  with  $\text{NO}_2$ , only alkyl nitrate  $\text{RONO}_2$  could be formed. Polarographic analysis does not permit separation of  $\text{RONO}$  and  $\text{RONO}_2$  since both are reduced at the same half-wave potential. Therefore we made a spectrophotometric analysis of the products of the experiment which confirmed the presence of alkyl nitrite in them. Then the amount of alkyl nitrite determined spectrophotometrically was equal to the polarographically determined sum of nitrite and nitrate, that is, actually only alkyl nitrite occurred in the product. This indicates the incorrectness of the Gray theory of the splitting of nitrite at the moment of its formation from  $\dot{R}$  and  $\text{NO}_2$ . It is evidently possible to distribute the excess energy along the bonds (without breaking them) and later to dissipate it in deactivating collisions

alkoxyl radical and  $\text{NO}$  which results from the reaction of  $\text{NO}_2$  with  $\text{H}$  atoms. However, specially run experiments to study the reaction of known  $\text{C}_2\text{H}_5\text{ONO}$  with  $\text{H}$  atoms (but without  $\text{NO}_2$ ) showed that in this case aldehyde and  $\text{CO}$  were also obtained. Also, it was found that  $\text{CH}_3\text{NO}_2$  reacts with atomic  $\text{H}$  and the degree of transformation under our conditions reached 60%.

Thus, as a test of the Gray hypothesis and an understanding of the true relation between the formation of  $\text{RNO}_2$  and  $\text{RONO}$  it is necessary to carry out a study of the reaction  $\dot{R} + \text{NO}_2$  in the absence of an excess of  $\text{H}$  atoms. This was done by separating the point of inlet of nitrogen dioxide from the point at which ethylene and atomic hydrogen were introduced by 90 mm and increasing the amount of added ethylene to  $\text{P}_{\text{C}_2\text{H}_4} = 0.16$  mm and reducing the current strength in the discharge tube to 0.07 a. All this reduced the concentration of atomic hydrogen at the point of meeting of  $\dot{R}$  with  $\text{NO}_2$ . We found that under such experimental conditions  $\text{CO}$ ,  $\text{CO}_2$ , and aldehyde were absent from the reaction products; this means that the reaction of  $\text{RONO}$  with atomic hydrogen did not occur.

In order to show the absence under these conditions of a reaction of atomic hydrogen with  $\text{RNO}_2$ , we added known  $\text{CH}_3\text{NO}_2$  to the reaction in mixture, with  $\text{NO}_2$ . As Table 2 shows, the amount of  $\text{CH}_3\text{NO}_2$  found in such experiments equalled the sum of the amount formed in ordinary experiments (that is, without addition of  $\text{CH}_3\text{NO}_2$ ) under the same conditions, and that artificially added.

Thus, under these experimental conditions there is no reaction of atomic hydrogen with either the nitroparaffin or the alkyl nitrite.

The results of the two series of experiments carried out at four different temperatures are given in Table 3.

$\text{CO}$ ,  $\text{CO}_2$ , and  $\text{HCHO}$  are absent from the products of all the experiments at all temperatures (at 96° traces of aldehyde were found qualitatively in the dimedon

By the use of the relation of the ratio  $RNO_2/RNO$  to temperature, we can determine the energy of activation difference in the two paths of reaction of  $\dot{R}$  with  $NO_2$ , which equals 1 kcal/mole (Fig. 1 and Table 4). From this relation we find the ratio of steric factors  $f_2/f_1 \approx 0.6$ .

Thus, the formation of alkyl nitrite requires somewhat greater energy of activation and has a greater steric factor than for the formation of the nitroparaffin.

To test the role of surface in the reaction  $\dot{R} + NO_2$  we carried out experiments in a reactor whose surface was covered with KCl or  $K_2B_4O_7$ . No change in composition or amount of products was found, which indicates the homogeneous character of the reaction of alkyl radicals with nitrogen dioxide (Table 5).

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## DIACYL DERIVATIVES OF PHENYLHYDRAZINE. THE QUESTION OF THE RELATION OF CHEMICAL STRUCTURE AND ANALGESIC ACTION

Z. V. Pushkareva and N. I. Latosh

(Presented by Academician L. N. Nazarov, November 20, 1956)

The struggle against pain has attracted attention during all human history and the field of anesthetic agents has developed greatly, especially in the last 15-20 years [1-4]. However, the analgesic agents used in present day medicine, including antipyrine and pyramidon, have certain deficiencies which arise from their harmful side effects on the human organism.

In 1929 R. Charonnat and R. Delaby [5] attempted to reduce the toxicity of pyramidon by preparing the N-oxide. When pyramidon (I) was oxidized with hydrogen peroxide it gave a product which had the analgesic activity of pyramidon and much less toxicity, but it was not the expected N-oxide; it was  $\alpha$ -dimethylamidooxalyl- $\beta$ -methyl- $\beta$ -acetylphenylhydrazine, or the so-called dioxypyramidon (II).

This induced us to synthesize a series of diacyl derivatives of phenylhydrazine with the general formula (III) and to study in them the connection between chemical structure and analgesic action.

The first group of compounds to be synthesized consisted of "skeletal" substances, in which  $R_1$ ,  $R_2$ , and  $R_3$  were methyl and phenyl groups in all possible combinations (IV), (V), (VI), (VII), (VIII), and (IX).

The study of these simple substances led us to study the effect of comparatively simple structural changes in the  $\alpha$ - and  $\beta$ -acyl groups of phenylhydrazine on the properties of the molecule.

The second group of compounds belonged to the derivatives of  $\alpha$ -benzoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (VII). When we introduced different substituents into the benzene ring of radical  $R_1$ , we obtained a number of substances structurally related to it (general formula X) with which to study the effect of different substituents united with the  $\alpha$ -acyl group on the properties of the molecule as a whole (XI), (XII), (XIII). Since among these compounds there was no benzoyl derivative with electron-acceptor substituents in the ring, we synthesized  $\alpha$ -isonicotinoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XIV).

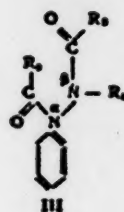
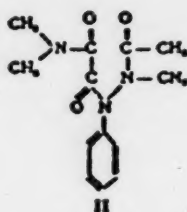
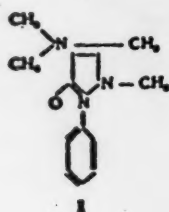
In addition to the second group of substances we obtained compounds (XV) and (XVI) in which the  $\alpha$ -acyl radical also contained a phenyl group which was not connected directly to the carbonyl group, but was separated from it. In one case (XVI) the separating group was the conjugated connection ( $-\text{CH}=\text{CH}-$ ), and in the other (XV) a group which broke the conjugation ( $-\text{CH}_2-$ ).

Finally, compound (XV) was like a partly hydrogenated dioxypyramidon (II) and contained in the  $\alpha$ -position instead of the oxamido group, a dialkylaminoacetyl group.

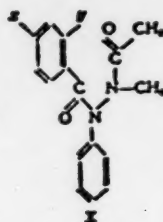
The sources for synthesis of all the enumerated compounds were either phenylhydrazine or hydrazobenzene, and from these the substances were obtained by one of two paths.

Investigators who have worked with the most studied form of the diacylhydrazines, dioxypyramidon [5, 6] have noted its poor ability to crystallize, though it has a high enough melting point (105°). Strictly speaking, the difficulty is connected with obtaining the first crystals, and further recrystallizations with seeding go sufficiently smoothly. To a greater or less degree this difficulty is found in all our diacyl derivatives of phenylhydrazine, either alkylated or nonalkylated, while the monoacyl products (XVIII etc.) were easily crystallized and purified. Therefore we preferred to use the second scheme in the synthesis. Also,  $\beta$ -methyl- $\beta$ -acetylphenylhydrazine (XVIII) is found in the skeleton of the molecules of most of the substances which were synthesized.

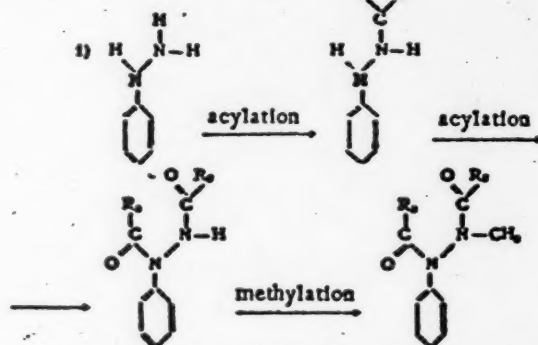
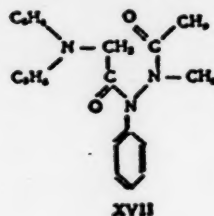
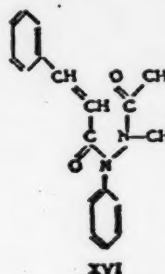
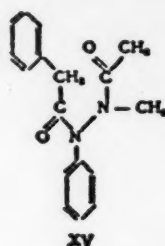
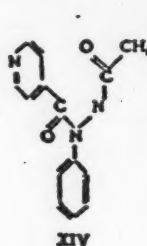




- IV  $R_1 = R_2 = R_3 = CH_3$   
 V  $R_1 = R_2 = CH_3$ ;  $R_3 = C_6H_5$   
 VI  $R_1 = CH_3$ ;  $R_2 = R_3 = C_6H_5$   
 VII  $R_1 = C_6H_5$ ;  $R_2 = R_3 = CH_3$   
 VIII  $R_1 = R_2 = C_6H_5$ ;  $R_3 = CH_3$   
 IX  $R_1 = R_2 = R_3 = C_6H_5$



- XI  $x = N(CH_3)_2$ ;  $y = H$   
 XII  $x = Br$ ;  $y = H$   
 XIII  $x = H$ ;  $y = OH$



(In the case of derivatives of hydrazobenzene the last step was excluded).

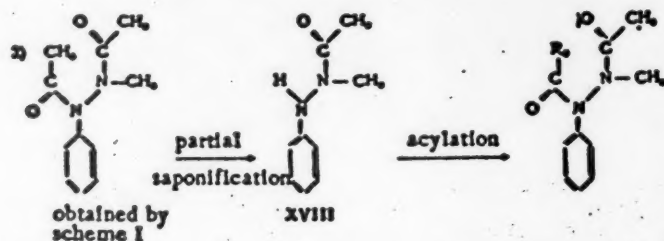




TABLE 1

Substance	Yield, % of theory	Brief characterization	Substance	Yield, % of theory	Brief characterization
N-Benzoyl-N'-acetylhydrazobenzene (VIII)	89.0	White crystals from alcohol, m. p. 149° Found %: N 8.32 Calculated %: N 8.48	$\alpha$ -Phenylacetyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XV)	53.0	White crystals from alcohol, m. p. 82° Found %: N 9.40 Calculated %: N 9.63
$\alpha$ -(p-Diethylamino)-benzoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XI)	86.0	Fine white crystals from 50% alcohol, m. p. 154° Found %: N 13.41 Calculated %: N 13.50	$\alpha$ -Cinnamoyl- $\beta$ -acetylphenylhydrazine	75.0	Fine white needles from alcohol, m. p. 143° Found %: N 10.22 Calculated %: N 10.04
$\alpha$ -p-Bromo- $\beta$ -benzoyl-acetylphenylhydrazine	80.0	White needles from alcohol, m. p. 168° Found %: N 8.50 Calculated %: N 8.67	$\alpha$ -Cinnamoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XVI)	92.0	White needles from alcohol, m. p. 123° Found %: N 9.74 Calculated %: N 9.52
$\alpha$ -(p-Bromo-benzoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XII)	75.0	White needles from 70% alcohol, m. p. 126° Found %: N 8.42 Calculated %: N 8.31	$\alpha$ -Diethylaminoacetyl- $\beta$ -acetylphenylhydrazine	56.0	White needles from acetone, m. p. 80° Found %: N 15.78 Calculated %: N 15.97
$\alpha$ -(o-Hydroxy)-benzoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XIII)	73.0	Fine white crystals from benzene, m. p. 180° Found %: N 9.98 Calculated %: N 9.86	$\alpha$ -Chloroacetyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine		White crystals from alcohol, m. p. 62° Found %: N 11.39 Calculated %: N 11.64
$\alpha$ -Isocotinoyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XIV)	43.0	White crystals with brownish tint, from alcohol, m. p. 165° (hydrochloride m. p. 173°) Found %: N 15.44 Calculated %: N 15.61	$\alpha$ -Diethylaminoacetyl- $\beta$ -acetyl- $\beta$ -methylphenylhydrazine (XVII)	42.0	Thick, colorless liquid, b. p. 160-161°/5 mm Found %: N 15.33 Calculated %: N 15.16

In the process of the syntheses we studied the optimum conditions for partial deacylation [7], which permitted us to obtain (XVII) in 85-80% yields.

The brief data on the properties of the synthesized compounds which have not been described before are given in Table 1. Some of the substances were prepared by the methods described in the literature, (IV) [8], (V) [8], (VI) [9], (VII) [10], (IX) [11], and (XVIII) [7].

The results of the comparative study of physicochemical properties (ultraviolet spectra, dipole moments) of the synthesized compounds will be published separately. At the same time the substances were given to the Department of Pharmacology of the Sverdlovsk State Medical Institute for a study of their analgesic action. Preliminary results of the pharmacological study [12] show that substances of the type X have the most intensive activity.

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\*Original Russian pagination. See C. B. Translation.

\*\*In Russian.

## SELECTIVE CATALYTIC DEHYDROGENATION OF HIGH MOLECULAR-WEIGHT SATURATED HYDROCARBONS IN THE LIQUID PHASE

S. R. Serglenko, E. V. Lebedev, and A. A. Petrov

(Presented by Academician A. A. Balandin, July 18, 1958)

The reaction of catalytic dehydrogenation discovered by N. D. Zelinskii [1] has been widely applied in the study of the chemical nature of cycloparaffin hydrocarbons which are found in the light fractions of petroleum. However, until the present there has been no report on the use of this reaction for explaining the structure of the high molecular-weight saturated petroleum hydrocarbons.

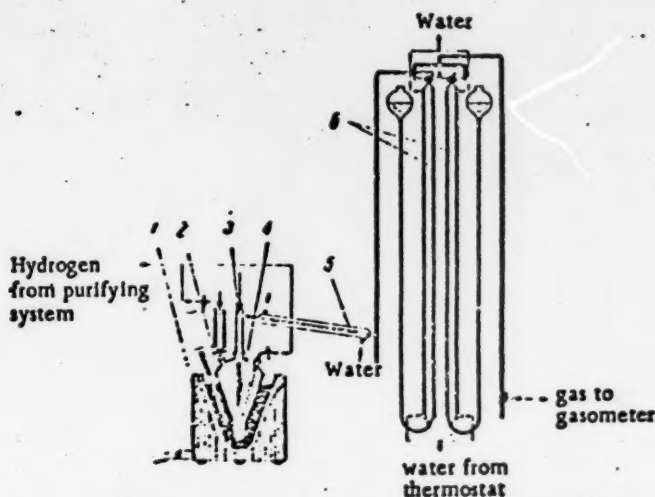


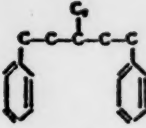
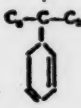
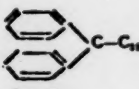
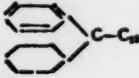
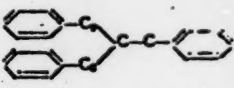
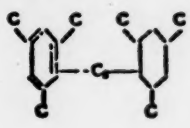
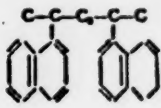
Fig. 1. Apparatus for dehydrogenation in the liquid phase.  
1) Metal bath for heating, 2) reaction vessel, 3) buret for hydrocarbons, 4) well for thermocouple, 5) condenser, 6) buret for measuring gas.

In carrying out a systematic study of the chemical nature of the high molecular-weight hydrocarbons of petroleum we decided to test the applicability of the reaction of selective catalytic dehydrogenation to explain the structure of these compounds. For this purpose we used synthetic hydrocarbons  $C_{20}$ - $C_{32}$  which contained in their molecules 1-3 cyclohexane rings, 2 decalin rings, 1 cyclopentane ring, and one paraffin with normal structure. First we found the optimum conditions for catalytic dehydrogenation of high molecular-weight cycloparaffin hydrocarbons in the liquid phase and an apparatus was built for carrying out the dehydrogenations (Fig. 1).

TABLE 1

Dehydrogenation of Individual Hydrocarbons and Their Mixtures (315°, Catalyst, Pt on Carbon (18%))

Exper. No.	Starting synthetic saturated hydrocarbon						Obtained by	
	Name	Structure	Empirical formula	M. p. °C	$n_D^{20}$	$d_4^{20}$		
							Yield, wt. %	
1	1,5-Dicyclohexyl-3-heptyl-pentane		$C_{24}H_{48}$	—	1.4776	0.8691	95.3	
2	n-Tetracosane	$-D-C_{24}$	$C_{24}H_{50}$	50.6	1.4288 <sup>70°</sup>	0.7682 <sup>70°</sup>	1.8	
3	n-Octadecylcyclopentane		$C_{23}H_{46}$	28.0	1.4543 <sup>70°</sup>	0.8211 <sup>70°</sup>	6.1	
4	Mixture of substance No. 1 (20%) and substance No. 2 (80%)	—	—	—	1.4360 <sup>70°</sup>	0.7816 <sup>70°</sup>	17.2*	
5	Mixture of substance No. 1 (70%) and sub. No. 2 (30%)	—	—	—	1.4470 <sup>70°</sup>	0.8145 <sup>70°</sup>	65.2**	
6	7-Cycloheptyloctadecane		$C_{21}H_{42}$	—	1.4630	0.8317	94.0	
							a) 96.0	
7	1,1-Dicyclohexyldodecane		$C_{21}H_{40}$	—	1.4803	0.8758	b) { I Fr. 33.8 II Fr. 35.3	
8	1,5-Dicyclohexyl-3-hexahydrobenzylpentane		$C_{34}H_{64}$	—	1.4920	0.9037	93.1	
9	1,2-Di-(1,3,5-trimethylcyclohexyl) ethane		$C_{26}H_{50}$	—	1.4788	—	94.5	
10	2,11-didecahydronaphthyl-dodecane		$C_{37}H_{70}$	—	1.5115	0.9484	23.8 59.1	

Aromatic hydrocarbon								
dehydrogenation of saturated hydrocarbon			Synthetic					Duration of dehydrogenation reaction, hours
M. p. °C	$n_D^{20}$	$d_4^{20}$	Name	Structure	M. p. °C	$n_D^{20}$	$d_4^{20}$	
—	1.5250	0.9249	1,5-Diphenyl-3-heptylpentane		—	1.52400	0.9233	20
—	1.4760 <sup>70*</sup>	—	—	—	—	—	—	20
—	1.5043 <sup>30*</sup>	—	—	—	—	—	—	20
—	1.5233	0.9235	—	—	—	—	—	20
—	1.5241	0.9239	—		—	1.4800	—	4
—	1.4803	—	7-Phenyloctadecane					
—	1.5242	0.9299	1,1-Diphenyldodecane		—	1.5241	0.9298	10
—	1.4980	0.8960	1-Phenyl-1-cyclohexyldodecane		—	1.4980	0.8960	0.5
—	1.5242	0.9248	—	—	—	—	—	—
35.9***	—	—	1,5-Diphenyl-3-benzylpentane		56.0	—	—	6
118****	—	—	1,2-Di-(1,3,5-trimethylphenyl)ethane		118	—	—	4
—	1.5455	—	—	—	—	—	—	—
—	1.5063	1.0197	2,11-dinaphthyldodecane		—	1.5060	1.0103	8

\*Yield based on 1,5-dicyclohexyl-3-heptylpentane in the mixture 80%.

\*\*Yield based on 1,5-dicyclohexyl-3-heptylpentane in the mixture 93.2%.

\*\*\*Mixed m. p. with 1,5-diphenyl-3-benzylpentane gave no depression.

\*\*\*\*Mixed m. p. with 1,2-di-(1,3,5-trimethylphenyl)ethane gave no depression.



## EXPERIMENTAL

The catalyst, Pt on carbon, was prepared according to B. A. Kazanskii [2] in the amount of 15-18% of the substance to be dehydrogenated, and was placed in flask 2 (Fig. 1) and reduced in a stream of hydrogen with slow heating to 320° (2-3 hours). Then the catalyst was kept for another hour at 315°. After this the hydrocarbon was added in the liquid phase from buret 3 into the reaction flask which was kept at the constant reaction temperature (315°). Addition of hydrogen to the system was stopped and the entire system was isolated. The gas which formed as a result of the dehydrogenation was cooled to 20° by passing through the condenser and measured in two burets which operated alternately, thermostatically controlled at 20°. When a buret was filled, the gas was transferred to a gasometer.

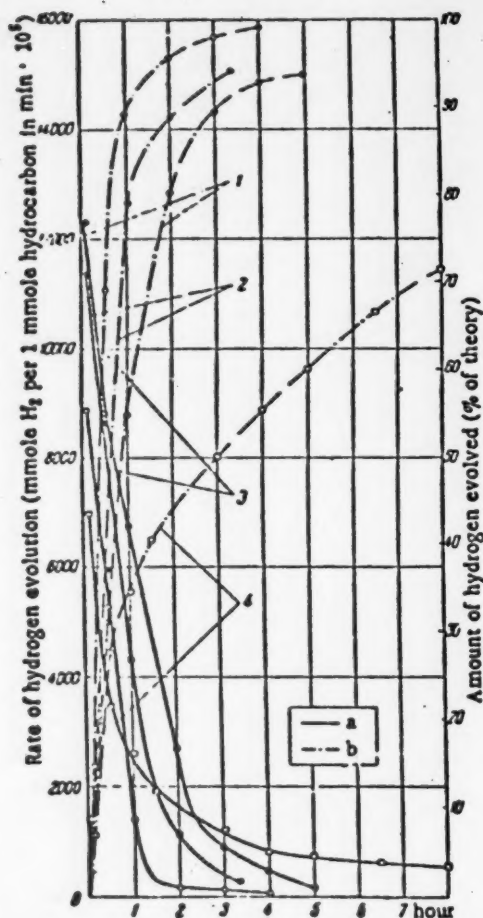


Fig. 2. Change in rate of evolution of hydrogen (a) and its total amount with time (b) in the dehydrogenation of individual hydrocarbons. 1-1, 5-Dicyclohexyl-3-hexahydrobenzylpentane, 2-1,2-di-(1,3,5-trimethylcyclohexyl)pentane, 3-7-cyclohexyloctadecane, 4-2,11-didecahydronaphthylododecane.

In order to determine the behavior of hydrocarbons with different structures under the conditions of a selective catalyst for dehydrogenation, we synthesized the following individual compounds: n-tetradecane, n-octadecylcyclopentane, 7-cyclohexyloctadecane, 1,5-dicyclohexyl-3-heptylpentane, 1,1-dicyclohexyldodecane, 1,5-dicyclohexyl-3-hexahydrobenzylpentane, 1,2-di-(1,3,5-trimethylcyclohexyl)ethane, and 2,11-didecahydronaphthylododecane.

Compounds which contained the isolated cyclohexyl and decaline structures were obtained by hydrogenation of the corresponding phenyl and naphthyl hydrocarbons which were prepared by the Grignard reaction. The syntheses of these individual hydrocarbons will be reported separately.

It was observed that the dehydrogenation of individual hydrocarbon homologs of cyclohexane and decaline occurred even at 280°, but the optimum temperature for dehydrogenation in the liquid phase in the presence of a platinum catalyst is a temperature of 315-320°. At this temperature dehydrogenation of all the hydrocarbons studied, whether they contained isolated or condensed hexamethylene structures, was complete in 5-6 hours with almost complete absence of cracking.

In Fig. 2 we show the change in rate of hydrogen evolution and the total amount of it with time for individual hydrocarbons with different structures. The reaction temperature in all cases was 315°.

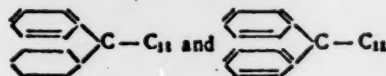
The liquid reaction products of the dehydrogenation were separated chromatographically on silica gel.

In Table 1 we give the results of catalytic dehydrogenation of individual hydrocarbons and their mixtures.

The investigation showed that the rate of hydrogen evolution in the dehydrogenation of hydrocarbons of various structures leveled off after 5-6 hours and became very slight, that is, the reaction was practically complete. An increased number of isolated hexamethylene rings in the hydrocarbon molecule and the presence of methyl groups in them affected the dehydrogenation process very little.

Compounds which contained two condensed hexamethylene structures were dehydrogenated with more difficulty.

In the dehydrogenation of 1,1-dicyclohexyldodecane, besides the full dehydrogenation, we carried out an experiment in which the dehydrogenation reaction was broken off at the moment when the amount of hydrogen evolved was about  $1/2$  of the theoretical. Chromatographic separation of the reaction products from this experiment showed that they contained about equal amounts of a) the starting 1,1-dicyclohexyldodecane, b) the product of complete dehydrogenation of both cyclohexane rings to benzene rings (1,1-diphenyldodecane), and c) the product of half dehydrogenation, 1-phenyl-1-cyclohexyldodecane. This result is experimental confirmation that the dehydrogenation of the cyclohexane ring goes simultaneously in both directions with formation of



The normal paraffin hydrocarbons under these conditions give a yield of 1.8% aromatic hydrocarbons which indicates the slight role of dehydrocyclization of the paraffin chain.

In studying n-octadecylcyclopentane under conditions of liquid-phase dehydrogenation we found formation of 6.1% of aromatic hydrocarbon. Condensation reactions in all cases were practically completely absent.

The study of the behavior of different structural groups of high molecular-weight saturated hydrocarbons under the conditions of liquid-phase dehydrogenation in the presence of Pt deposited on carbon and passivated Fe showed that the method of selective catalytic dehydrogenation in the liquid phase can be used successfully in studying the high molecular-weight saturated hydrocarbon fractions of petroleum, whose molecules contain cycloparaffin rings, for a more detailed characterization of their chemical nature.

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Received June 17, 1958

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# THE SYNTHESIS OF THE ALKALOID CINCHONAMINE

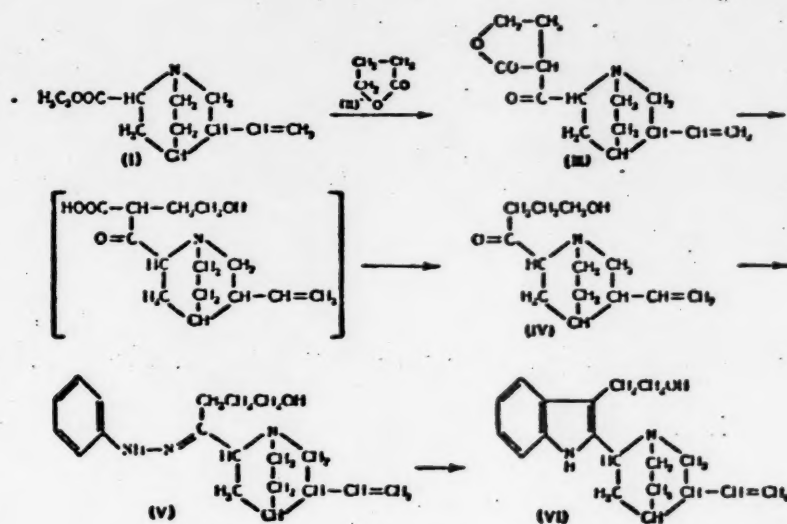
Ch'en Ch'ang-pai, R. P. Evstigneeva, and N. Preobrazhenskii

(Presented by Academician A. L. Oparin, July 31, 1958)

The alkaloid of cinchona root, cinchonamine, is the connecting link between the quinine alkaloids of the quinoline series and alkaloids of the indole series. This can be shown by direct synthetic transformation of dihydroquinine into 5-methoxydihydrocinchonamine [1] and of dihydrocinchonine into dihydrocinchonamine [2].

In the present communication we describe the synthesis of optically active cinchonamine.

The synthesis was carried out by a method which we worked out earlier for obtaining the pyridine analog of cinchonamine [3].



Ethyl 3-vinylquinuclidine 6-carboxylate (b. p. 80-82°/0.5 mm;  $n_D^{25}$  1.4350;  $d_4^{25}$  1.028;  $M_{rD}$  found 58.35, calculated 58.34,  $[\alpha]_D^{25} + 69.58^\circ$  at c 1.006, 95%  $C_2H_5OH$ ) (I) was condensed with  $\gamma$ -butyrolactone (b. p. 70.5-72°/5 mm,  $n_D^{25}$  1.4336) (II) in dry benzene in the presence of sodium ethylate at 40-85°. After the corresponding treatment we obtained  $\alpha$ -(3-vinyl-6-quinuclidoyl)- $\gamma$ -butyrolactone (III) in the form of a colorless, viscous, oily substance, easily soluble in ether, alcohol, benzene, and water. B. p. 152-153°/0.5 mm. Yield 35.7%.

Found %: C 67.21; 67.32; H 7.96; 7.98; N 5.61  
 $C_{14}H_{19}O_3N$ . Calculated %: C 67.45; H 7.68; N 5.62

Reineckate m. p. 152.5-154° (with decomposition).

Found %: C 38.21; 38.35; H 4.43; 4.74; N 17.20; 17.14  
 $C_{14}H_{19}O_3N \cdot C_4H_7N_6S_6Cr$ . Calculated %: C 38.03; H 4.61; N 17.25

When compound(III) was heated with 2N sulfuric acid at 120°, the lactone ring opened and was decarboxylated with formation of  $\omega$ -hydroxypropyl- $\alpha$ -(3-vinyl-6-quinuclidyl)-ketone (IV). Yield 70.3%.

The resulting light yellow liquid was heated with a 10% alcoholic solution of phenylhydrazine for 8 hours. The resulting phenyl hydrazone of  $\omega$ -hydroxypropyl- $\alpha$ -(3-vinyl-6-quinuclidyl)-ketone (V) was a thick yellow oil. Yield 76.5%.

The reineckate after recrystallization from aqueous alcohol had m. p. 136.5-138° (with decomposition)

Found %: C 43.36; H 5.28

$C_{21}H_{27}ON_3 \cdot C_6H_7N_3S_2Cr$ . Calculated %: C 43.65; H 5.42

To the phenylhydrazone (V) in anhydrous ethyl alcohol was added twice its amount of concentrated sulfuric acid and the mixture was heated for an hour at 60° [4]. Then it was neutralized with an alcoholic solution of ammonia, the ammonium sulfate was separated, the alcohol was distilled off, the base was isolated with potash and removed by ether. After the solvent had been removed, the light-yellow oil was treated with alcohol to give cinchonamine in the form of colorless crystals, easily soluble in hot alcohol, ether, chloroform, and benzene, less so in cold alcohol, and poorly soluble in petroleum ether and water.

M. p. 196°.  $[\alpha]_D^{25} + 120^\circ$  (C 0.203, 96%  $C_2H_5OH$ ).

$\lambda_{max}(C_2H_5OH)$  250  $m\mu$  (log  $\epsilon$  3.98)

$\lambda_{max}(C_2H_5OH)$  247  $m\mu$  (log  $\epsilon$  3.71)

The constants of our synthesized optically active cinchonamine fully agree with those described in the literature for the natural alkaloid [5].

Our reactions which lead to the synthesis of cinchonamine open the way to the preparation of other alkaloids of this series.

M. V. Lomonosov Moscow Institute of  
Fine Chemicals Technology

Received July 30, 1958

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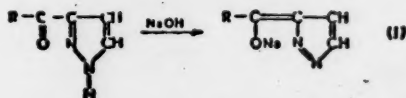


## THE ACID PROPERTIES OF 3-ACYLPYRAZOLES

Iu. N. Sheinker, Ivan Ambrush, and N. K. Kochetkov

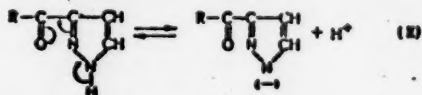
(Presented by Academician A. N. Nesmelanov, July 1, 1958)

According to the data of A. N. Nesmelanov and N. K. Kochetkov, who worked out a satisfactory method of synthesis, the 3-acylpyrazoles, as distinct from pyrazole and its homologs, have the properties of weak acids [1]. To explain this effect we made the assumption that salt formation is accompanied by a tautomeric shift of the double bonds with destruction of the aromatic system of pyrazole and formation of an O-metallic derivative according to the equation



In support of this idea is the known high electronegativity of the oxygen atom compared to the nitrogen so that the negative charge should be centered preferably on the oxygen atom. A number of cases are described in the literature in which, in compounds with the system of double bonds  $\text{O}=\text{C}-\text{C}=\text{N}-\text{NH}$  [2] or  $\text{O}=\text{C}-\text{C}=\text{C}-\text{NH}$  [3-5], salt formation is connected with a shift in the bonds. A study carried out earlier in our laboratory [6] showed that in the ultraviolet absorption spectrum of 3-acylpyrazolones there was a considerable bathochromic shift with transfer from a neutral to an alkaline medium, which would indicate a change in the system of  $\pi$ -electrons in the molecule. At the same time, for 3,5-diphenyl-4-bromopyrazole, which also has acid properties but cannot undergo a tautomeric shift of bonds to destroy the aromatic system of pyrazole, this shift in the ultraviolet spectrum is not observed [7].

Another possible explanation of the acid properties of 3-acylpyrazoles is that under the influence of an electron-acceptor effect of the carbonyl group of the acyl radical which is connected to the nucleus, the N-H bond in the pyrazole ring is polarized, as a result of which the hydrogen can split off as a proton:



In favor of this assumption is the fact, known from the literature, that pyrazoles with negative substituents have acid properties [8-10].

Originally, on the basis of the study of the ultraviolet spectra of the acylpyrazoles, we were inclined to give preference to the first of these possible explanations [6], but these data did not permit a final choice between scheme I and II. For a final solution of the question of the nature of the acid properties of the acylpyrazoles we studied the infrared spectra of some compounds of this type and their metallic derivatives. In fact, if the frequency of the CO group were absent in the infrared spectra of the salts, as is the case with the infrared spectra of salts of  $\alpha$ - and  $\gamma$ -pyridones [11], then we could speak of the tautomeric shift with salt formation by scheme I; but if the frequency of the carbonyl group were kept in the infrared spectra of the salts, it would show positively that salt formation was by scheme II. We determined the infrared spectra of 3-acetyl-, 3-pivaloyl-, and 3-benzoylpyrazole and also the sodium and silver salts of 3-acetylpyrazole. The 3-acetylpyrazole was synthesized by the method which was worked out earlier in our laboratory [1, 12]. The sodium salt of 3-acetyl-

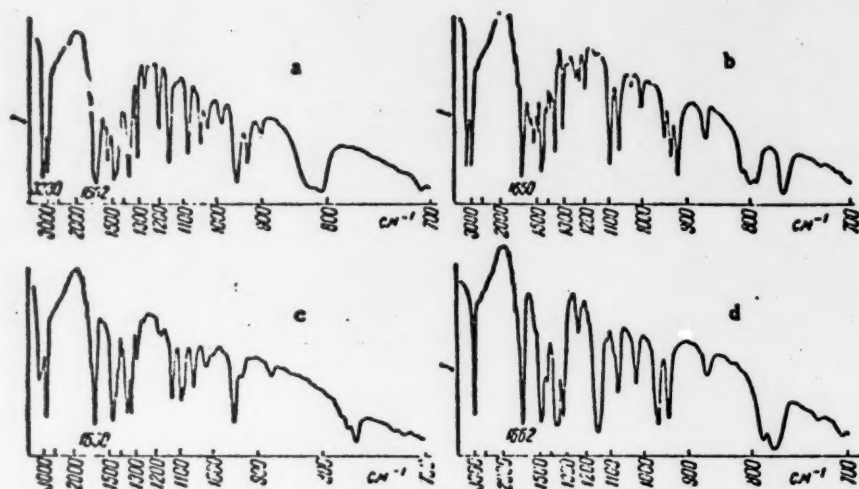


Fig. 1. Infrared spectra of 3-acetylpyrazole (a), 3-pivaloylpyrazole (b), sodium salt of 3-acetylpyrazole (c), and silver salt of 3-acetylpyrazole (d).

pyrazole was obtained in 78% yield by the action of sodium ethylate on 3-acetylpyrazole in alcohol solution, followed by precipitation with ether. The powdery salt contained 10-15% sodium alcoholate, but this has no significance for our purpose.

Found %: N 18.83; 18.46

$C_5H_5N_2ONa$ . Calculated %: N 21.21

The silver salt of 3-acetylpyrazole was obtained in 93% yield by the reaction of 3-acetylpyrazole with an aqueous ammonia solution of silver nitrate to form a curdy, colorless precipitate which was filtered and dried.

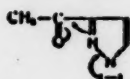
Found %: C 27.97; 27.90; H 2.48; 2.38; Ag 49.81; 49.51

$C_5H_5N_2OAg$ . Calculated %: C 27.67; H 2.32; Ag 49.71

The infrared spectra of all these substances were measured in an IKS-11 apparatus in the crystalline form (paste with vaseline oil); they are given in Fig. 1. As can be seen, in the infrared spectrum of 3-acetylpyrazole (Fig. 1a) there is an intense band, which corresponds to the oscillation of the  $C=O$  group at  $1662\text{ cm}^{-1}$  and an intense band at  $3230\text{ cm}^{-1}$  from the valence oscillation of the bond. It is interesting that the shift in the  $C=O$  band compared to the position in saturated ketones with open chains ( $1725\text{--}1705\text{ cm}^{-1}$ ) is stronger when the carbonyl group is on the pyrazole ring than when it is on the benzene ring (in acetophenone the frequency of the carbonyl band is  $1686\text{ cm}^{-1}$ ). An analogous and even greater effect, however, is found in p-aminoacetophenone ( $1634\text{ cm}^{-1}$ ) [13]. Evidently the explanation of such shifts in frequency is connected with the electron donor properties of the amino group which decreases the force constant of the  $C=O$  bond. In our opinion, the same explanation applies to the decreased frequency of the  $C=O$  band in 3-acetylpyrazole (see scheme II). This view is confirmed by the position of the carbonyl band in the infrared spectra of 3-pivaloylpyrazole ( $1650\text{ cm}^{-1}$ , see Fig. 1 b) and 3-benzoylpyrazole ( $1636\text{ cm}^{-1}$ ). The decrease in frequency in these cases is explained by the fact that besides the electrons supplied to the carbonyl group by the pyrazole ring there is a supplementary source of electrons from the tertiary butyl group (because of its +I effect) or from the benzene ring (because of its polarizability).

In the infrared spectrum of the sodium salt of 3-acetylpyrazole (Fig. 1c) there is an intense band for the carbonyl group at  $1650\text{ cm}^{-1}$  and at  $3000\text{--}3500\text{ cm}^{-1}$  (oscillation of the  $N-H$  bond), there is a strongly deformed, not very intense band. The latter was ascribed to the presence of contaminants. The presence of the intense carbonyl band excludes the possibility that the negative charge on the anion of the salt is centered chiefly on the oxygen atom. Hence, in the anion the negative charge is mainly centered on the nitrogen atoms (or on one of them). Support for this idea comes from the fact that the frequency of the carbonyl group in the spectrum of the

salt undergoes a supplementary shift. This effect can be explained by the fact that the pyrazole ring in which one of the nitrogen atoms bears a negative charge is more able to give up an electron than a "neutral" ring:



If we consider the infrared spectrum of the silver salt of 3-acetylpyrazole (see Fig. 1d), we find that it contains as intense a band at  $1662\text{ cm}^{-1}$  as does free 3-acetylpyrazolone. At the same time the band from the N-H bond vanishes completely. We can conclude from this that the silver atom replaces the hydrogen atom and forms a substance in which the N-Ag bond is covalent. In support of this idea is the fact that the oscillation frequency of the carbonyl group is exactly the same as in unsubstituted 3-acetylpyrazole, and so the effect found with the sodium salt of 3-acetylpyrazole, which depends on the charge on the nitrogen atom, is here absent.

Thus, the data presented in this paper force us to abandon the idea of salt formation by formation of O-metallic derivatives (scheme I) and along with it the earlier idea [6] of possible tautomerism of the 3-acylpyrazoles. It is clear that since the carbonyl group is present in the metallic derivatives of 3-acylpyrazoles, then salt formation in these compounds is connected with strengthening the polarization of the N-H bond of the pyrazole ring under the influence of the electron-acceptor effect of the acyl group (scheme II). It is evident, in spite of the great electronegativity of the oxygen atom, that the destruction of the aromatic character of the pyrazole ring when O-metallic derivatives are formed is so strongly hindered that salt formation on the nitrogen atom is the more favored process energetically. As to the above-mentioned bathochromic shift in the ultraviolet spectrum of 3-acylpyrazoles in an alkaline medium, this in all probability is connected with some deformation of the system of  $\pi$ -electrons of the pyrazole ring, which is confirmed by the above-noted shift in the bands of the C=O group in the infrared spectra of salts of 3-acetylpyrazole.

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Received June 25, 1958

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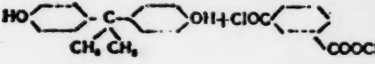
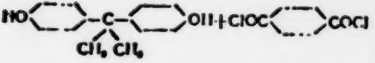
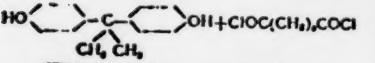
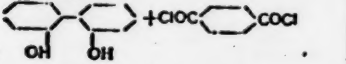
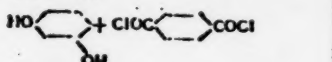
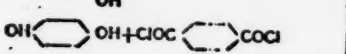
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# KINETICS OF DIACYLCHLORIDE POLYCONDENSATION WITH DIHYDRIC PHENOLS\*

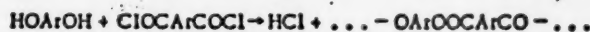
S. V. Vinogradova and Corresponding Member Acad. Sci. USSR V. V. Korshak

A double decomposition (one example of which is the reaction between acyl chlorides of dicarboxylic acids and diols) is one of the least studied cases of polyesterification. The literature contains only scant references on the preparation of ethers by this reaction [1-6].

TABLE 1

Starting materials	Reaction Temperature, °C	Rate constant, liter/mole·sec·10 <sup>3</sup>	The degree of completion (of reaction) after 7 hours
	150	5.72	0.17
	170	10.7	0.26
	180	17.99	0.38
	200	50.3	0.63
	210	92.0	0.72
	150	2.99	0.09
	170	6.56	0.17
	180	14.3	0.33
	190	30.4	0.46
	210	79.6	0.64
	150	344	—
	170	6.9	0.16
	170	7.06	0.19
	170	11.7	0.27

In a preceding communication [7] we reported some data on the polyesters of aromatic dicarboxylic acids and dihydric phenols. The aim of the present work was to investigate the kinetics of the polyester formation, which proceeds as follows:



Polycondensation kinetics were studied by the use of the following representative reactions: isophthalyl and terephthalyl dichlorides with p,p'-dihydroxyphenylpropane in the 150-210° range; terephthalyl dichloride with o,o'-dihydroxydiphenyl, resorcinol, and hydroxyquinone at 170°; sebacoyldichloride with p,p'-dihydroxydiphenylpropane at 150°. The reactions were carried out in a dilindanyl solution in a current of purified dry nitrogen and with equimolar amounts of starting materials. In the majority of experiments we used 200 ml of dilindanyl, 2.67 g of aromatic acyl chloride and a corresponding amount of diol. The course of the reaction was

\*V. S. Arteinova and D. T. Morozova participated in the experimental work.



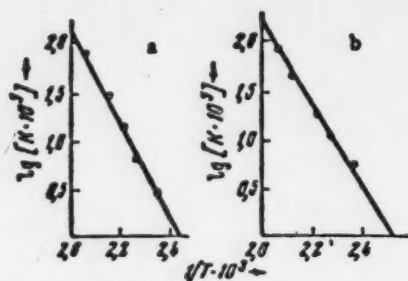


Fig. 1. The dependence of rate constants on temperature in the reactions between p,p'-dihydroxydiphenylpropane and: 1) terephthalyl dichloride; 2) isophthalyl dichloride.

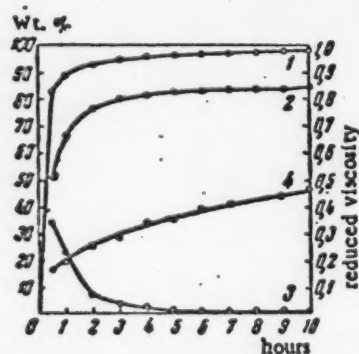


Fig. 2. Kinetics of the isophthalyl dichloride polycondensation with p,p'-dihydroxydiphenylpropane at 220°: 1) change in the amount of hydrogen chloride evolved during the reaction; 2) change in the quantity of polyester in the reaction mixture; 3) change in the quantity of starting materials and low molecular-weight polyesters in the reaction mixture; 4) change in the reduced viscosity of polyester.

checked by determining the quantity of hydrogen chloride evolved in the reaction. In some experiments we took out samples of reaction mixture during the reaction so as to determine the amount and viscosity of the polymer in the mixture.

The order of the reaction between isophthalyl dichloride and p,p'-dihydroxydiphenylpropane was determined by the Van't Hoff method [8] and indicated a bimolecular reaction mechanism. The rate constants of this and other reactions were calculated with a second-order rate equation and remained unchanged during the whole reaction, which also confirmed the bimolecular reaction mechanism.

Table 1 lists the data on the rate constants and degrees of completion in the reaction between acyl chlorides and diols.

In the reaction between p,p'-dihydroxydiphenylpropane and terephthalyl and isophthalyl dichlorides the change in the rate constant obeys Arrhenius equation, as may be seen in Fig. 1. A treatment of the experimental data by the method of least squares gave the following Arrhenius Equations:  $\log K = 7.13 - 4963/T$  and  $\log K = 5.81 - 4308/T$  respectively. According to these equations the activation energy for the reaction between isophthalyl dichloride and p,p'-dihydroxydiphenylpropane is 19,700 cal with a frequency factor of  $0.646 \cdot 10^6$ . For the terephthalyl dichloride and p,p'-dihydroxydiphenylpropane the activation energy is 22,700 cal with a frequency factor of  $0.135 \cdot 10^6$ . The higher frequency factor in the reaction of terephthalyl dichloride with p,p'-dihydroxydiphenylpropane can obviously be explained by a steric effect. Since the reacting groups in isophthalyl dichloride are meta to each other, the approach of the other molecule is more hindered than in the case of para position on the ring. This in turn decreases the collision frequency between acyl chlorides and hydroxyl groups in the polyesterification of isophthalic acid. From the graph of rate constant vs. temperature for the reaction of p,p'-dihydroxydiphenylpropane with terephthalyl and isophthalyl dichlorides we calculated reaction temperature coefficients (see Table 2).

TABLE 2

Starting materials	Temperature (in °C) ratios					
	$\frac{160}{150}$	$\frac{170}{160}$	$\frac{180}{170}$	$\frac{190}{180}$	$\frac{200}{190}$	$\frac{210}{200}$
$\text{HO} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}(\text{CH}_2)_3 \text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{OH} + \text{ClOC} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{COCl}$	1,30	1,4	1,68	1,68	1,05	1,82
$\text{HO} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \end{array} \text{C}(\text{CH}_2)_3 \text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \end{array} \text{OH} + \text{ClOC} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{COCl}$	1,30	1,62	2,18	2,13	1,76	1,48

To explain the effect of structure (in the starting material) on the reaction rate it is necessary to compare the different reaction rate constants given in Table 1 with each other. As may be seen from the data in Table 1, isophthalyl dichloride reacts faster with p,p'-dihydroxydiphenylpropane than does terephthalyl dichloride. The replacement of an aromatic acyl chloride by an aliphatic increases the reaction rate considerably. Thus, sebacyl dichloride reacts at 150° with p,p'-dihydroxydiphenylpropane at a rate which is 60 times higher than that of isophthalyl dichloride and 115 times higher than that of terephthalyl dichloride.

The reaction rate depends also on the structure of the dihydric phenol used. At 170° p,p'-dihydroxydiphenylpropane, resorcinol, hydroquinone, and o,o'-dihydroxydiphenyl react with terephthalyl dichloride and the reaction rates decrease in the following order: hydroquinone > resorcinol > o,o'-dihydroxydiphenyl > p,p'-dihydroxydiphenylpropane. It should be noted here, that the differences in the reaction rates of the last three diols are small.

Table 1 lists the data on the degree of reaction completion after seven hours. It may be seen that with increase in reaction temperature the degree of completion increases. However, even if the reaction between p,p'-dihydroxydiphenylpropane and isophthalyl dichloride is carried out at 210° the degree of completion is only .72, i. e. only 72% of material has reacted.

In this case the change in the reduced viscosity of polymer (in cresol) was determined in the course of reaction and turned out to be small; between the 2nd and 10th hour of the reaction it hardly changed at all, remaining equal to ~ 0.18. In order to increase the degree of completion we studied the reaction between p,p'-dihydroxydiphenylpropane and isophthalyl dichloride at a higher temperature (220°) and with higher initial concentrations of reactions (we took 5 g of diol and 4.45 g of acyl chloride in 100 ml of diindanyl). It turned out that after 7 hours the degree of completion was 0.975 - a considerable increase.

In Fig. 2 we have graphically represented the change in the composition of reaction mixture and the reduced viscosity of polyester during the course of reaction. It may be seen from Fig. 2 that in the course of reaction there is an uninterrupted increase in the reduced viscosity of polyester, i. e., in its molecular weight. The fact that after 3 hours the amount of polymer practically does not change, while the quantity of low-molecular component is already very insignificant by that time, undoubtedly indicates that after 3-4 hours the increase in the polymer chain is principally on account of a reaction between polymeric molecules themselves.

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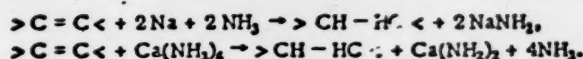
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## REDUCTION OF CONJUGATED DIENES WITH NASCENT HYDROGEN

I. V. Gostunskaya, N. I. Gusar\*, A. I. Leonova and Academician B. A. Kazanskii

Nascent hydrogen is capable of adding to diene hydrocarbons not only in the 1,4-position but also in the 1,2 or 3,4-positions [1-6]. The addition orientation depends on the diene structure: increased number of alkyl groups on the 1st or 4th (terminal) carbons of the conjugated system promotes 1,2 or 3,4 addition of hydrogen, while presence of alkyl groups on 2nd or 3rd atoms of conjugated systems helps 1,4-addition. Thus isoprene and diisopropenyl (2,3-dimethylbutadiene-1,3) add nascent hydrogen almost exclusively in the 1,4-position, while diisocrotyl (2,5-dimethylhexadiene-2,4) and 2-methyl-hexadiene-2,4 mostly in the 1,2 and 3,4-positions.

When reduction is done with sodium in liquid ammonia [1-4] or with hexamminecalcium [5-6] metal amides are formed simultaneously with the addition of hydrogen to the double bonds:



As has recently become apparent, amides are capable of catalyzing double bond rearrangements in mono- and diolefinic hydrocarbons [7-10]. In this connection one would expect that under certain conditions the structure of the monoolefin formed after addition of one hydrogen molecule to a diene would depend not only on the structure of the original diene but also on the secondary isomerization influenced by the metal amide formed.

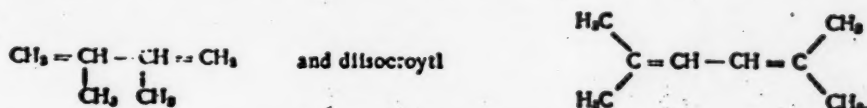
TABLE 1

Composition of Reduction Products in Wt. %

Starting diene	Monoolefin	Addition orientation	Reducing agent		
			Ca(NH <sub>2</sub> ) <sub>2</sub>	Na + NH <sub>3</sub>	Na + NH <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH
Diisopropenyl (2,3-dimethylbutadiene-1,3)	2,3-Dimethylbutene-1	1,2	9	2	4
	2,3-Dimethylbutene-2	1,4	91*	98 [3]	96*
Diisocrotyl (2,3-dimethyl-2,5-hexadiene-2,4)	2,5-Dimethylhexene-2	1,2	77	84	71
	2,5-Dimethylhexene-3	1,4	23 [5]	16*	29*

\*Data obtained in the present work.

In order to estimate the role of this possible secondary reaction we carried out a reduction of diisopropenyl



(these are the two extreme cases in the distribution of methyl groups with respect to the four carbons of the butadiene structure) under conditions which excluded the isomerizing action of metal amide. For this purpose we used as a reducing agent sodium and ethyl alcohol in liquid ammonia. As has previously been shown [11], the double bond is not displaced during partial reduction of heptene-1 and octene-1.

TABLE 2

Fract. No.	B. p., °C	Yield, wt. %	$n_D^{20}$	$d_4^{20}$
1	55,7-56,2	6,4	1,3892	0,6756
2	56,2-72,2	4,5	1,4055	0,7000
3	72,7-73,2	23,5	1,4139	0,7107
4	73,2	61,0	1,4144	0,7110

TABLE 3

Olefin	B. p., °C	$n_D^{20}$	$d_4^{20}$	Source
2,3-Dimethylbutene-1	55,67	1,3904	0,6779	[14]
2,3-Dimethylbutene-2	73,21	1,4122	0,7080	[14]

\*The boiling points in Tables 2-7 are given at 760 mm.

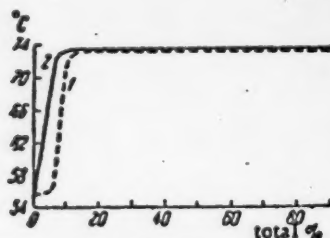


Fig. 1. Fractional distillation curves of diisopropenyl reduction products: 1) hexamminecalcium; 2) sodium and alcohol in liquid ammonia.

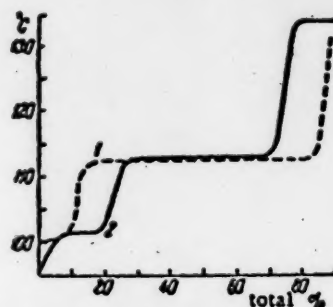


Fig. 2. Fractional distillation curves of diisocrotyl reduction products: 1) sodium in liquid ammonia; 2) sodium and alcohol in liquid ammonia.

TABLE 4

Fract. No.	B. p., °C	Yield, wt. %	$n_D^{20}$	$d_4^{20}$
1	56,7-60,3	1,4	1,3894	—
2	60,3-73,3	7,3	1,4068	—
3	73,3	63,2	1,4122	0,7089
Residue	—	18,1	1,4165	—

TABLE 5

Fract. No.	B. p., °C	Yield, wt. %	$n_D^{20}$	$d_4^{20}$
1	101,5-102,3	7,0	1,4020	0,7008
2	102,3-114,0	12,4	1,4090	0,7109
3	114,0	63,3	1,4150	0,7187
Residue	—	15,0	1,4718	0,7694

TABLE 6

Olefins	B. p., °C	$n_D^{20}$	$d_4^{20}$	Source
2,5-Dimethylhexene-2	112,2	1,4140	0,720	[14]
2,5-Dimethylhexene-3	102	1,406	0,710	[14]
(mixture of cis and trans)	103,5	1,4100	0,7122	[15]
	99,7-99,9	1,4040	0,7015	[16]

TABLE 7

Fract. No.	B. p., °C	Yield, wt. %	$n_D^{20}$	$d_4^{20}$	Fract. No.	B. p., °C	Yield, wt. %	$n_D^{20}$	$d_4^{20}$
1	96,5-101,5	7,5	1,4020	0,7063	5	113,0-134,4	4,9	1,4648	0,7597
2	101,5	12,7	1,4045	0,6998	6	134,4	16,8	1,4780	0,7628
3	101,5-113,0	6,4	1,4125	0,7142	Residue		7,0	1,4780	—
4	113,0	43,6	1,4155	0,7189					



Besides this, we reduced diisopropenyl with hexamminecalcium and diisocrotyl with sodium in liquid ammonia (under the same conditions as in the experiment with alcohol). The last reaction was already studied by Levina and co-workers [2], though under slightly different conditions (with higher sodium concentrations and longer reaction times).

The data on the reduction of the above-mentioned compounds obtained in the present work as well as that already listed in the literature are given in Table 1.

According to these data, diisopropenyl when reduced with all the investigated sources of nascent hydrogen undergoes almost exclusively 1,4 addition. The reduction of diisocrotyl is less selective, though hydrogen adds principally in the 1,2 position.

A comparison of the data obtained with hexamminecalcium and sodium in liquid ammonia (systems capable of causing double-bond rearrangement in monoolefins) with data obtained with sodium and alcohol in liquid ammonia shows that, although the secondary isomerization reaction changes somewhat the results of primary reduction, it does not alter them, and consequently the rules introduced in the works of Levina, Kazanskii and co-workers on the effects of diene structure on the reduction orientation still hold.

## EXPERIMENTAL

Reduction with sodium in liquid ammonia was carried out in a three-necked half-liter flask placed in a thermostat and supplied with a stirrer, dropping funnel, and tubes for introducing and removing ammonia. To 250 ml of liquid ammonia we added with vigorous stirring 0.4 g-at of sodium, and after that added the diene dropwise (0.2 moles) at  $-33^{\circ}$ . After all the diene was added the stirring was continued at the same temperature for two more hours, then 100 ml of dry ether were added to the flask, and the reaction mixture left till all the ammonia evaporated. On the following day the mixture was treated with water, the ether layer separated, washed with water, and dried over  $\text{CaCl}_2$ .

Reduction with sodium and ethyl alcohol in liquid ammonia was carried out in the above-described apparatus; to 0.4 g-at of sodium in 250 ml of liquefied ammonia we added a mixture containing 0.2 moles of diene and 0.8 moles of absolute ethyl alcohol. Mixing was continued till the mixture was decolorized, but not over 2 hours; further treatment was as already described.

Reduction with hexamminecalcium was carried out by a previously described method [5-12]. The molar Ca: diene ratio was 4:1.

Investigation of reaction products was carried out by fractional distillation in a column with 80 theoretical plates and by determination of properties of the fractions obtained.

## REDUCTION OF DIISOPROPENYL

Diisopropenyl was obtained by dehydration of 2,3-dimethylbutanediol-2,3 [13] and had a b.p.  $67.5^{\circ}$  at 760 mm,  $n_D^{20}$  1.4395,  $d_4^{20}$  0.7276,  $M_R$  29.67, found for  $\text{C}_5\text{H}_8$ ,  $F$ , 28.97;  $E$   $M_R$  0.70.

I. We reduced 75.4 g of diisopropenyl with hexamminecalcium. We obtained 57 g of hydrocarbon mixture, from which after boiling with maleic anhydride 39.4 g of olefin mixture was isolated. The results from the fractional distillation of the mixture are shown in Table 2 and Fig. 1.

The data from the fractionation curve and a comparison of properties of fractions with the properties of olefins which might have formed in the reduction of diisopropenyl (Table 3) showed that the reaction products contained about 9% of 2,3-dimethylbutene-1 and 91% 2,3-dimethylbutene-2.

II. We reduced 51 g of diene with sodium and alcohol in liquid ammonia; 24.9 g of reduction products were obtained. Properties of fractions obtained on distillation are given in Table 4, the fractionation curve is in Fig. 1.

In this case the principal reaction product was 2,3-dimethylbutene-2 with a small admixture of 2,3-dimethylbutene-1 whose contents according to our fractionation curves did not exceed 4%.

## REDUCTION OF DIISOCROTYL

Diisocrotyl was prepared from isomerization of diisobutenyl in the presence of calcium amide; b.p. 134.4° at 760 mm,  $n_D^{25}$  1.4780;  $d_4^{25}$  0.7627;  $M_R$  40.82, calculated for  $C_5H_{10}$ ,  $F_2$  38.21,  $M_R$  increment was 2.61.

I. We reduced 44.8 g of diisocrotyl with sodium in liquid ammonia; 38.7 g of hydrocarbon mixture was obtained. Fractionation curve is given in Fig. 2; properties of fractions obtained are listed in Table 5.

Comparison of properties of obtained fractions with the properties of octenes which might form in the reduction of diisocrotyl (Table 6) shows that fraction 1 corresponds to 2,3-dimethylhexene-3, fraction 3 to 2,5-dimethylhexene-2, and the residue in the flask to unreacted diisocrotyl.

The composition of the monoolefinic part of reduction products was calculated from the data in Table 6 and the fractionation curve and indicated the following amounts: 16% of 2,5-dimethylhexene-3 and 84% of 2,5-dimethylhexene-2.

II. We reduced 66 g of diene with sodium and alcohol in liquid ammonia and obtained 54.4 g of products. Fractionation curve is given in Fig. 2, properties of fractions in Table 7.

Fractions 1 and 2 corresponded to 2,5-dimethylhexene-3, fraction 4 to 2,5-dimethylhexene-2, fraction 6 and residue to unreacted diene. Composition of monoolefinic part was calculated and found to be 29% 2,5-dimethylhexene-3, 71% 2,5-dimethylhexene-2.

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## ALKYLATION OF TOLUENE BY $C_{10}$ OLEFINS IN THE PRESENCE OF SULFURIC ACID

Iu. I. Kozorezov and A. Z. Dorogochinskii

(Presented by Academician B. A. Kazanskii July 23, 1958)

In the manufacture of the most widespread group of synthetic wetting agents, alkylarylsulfonates, one usually uses the products of benzene alkylation by olefins with 10 to 15 carbon atoms.

However, due to an ever increasing demand for benzene in various chemical syntheses, it became necessary to study the possibilities of utilizing other aromatic hydrocarbons, in particular, toluene. One encounters in the literature [1, 3-7] isolated statements on the need of utilizing toluene in the preparation of alkylarylsulfonates, yet no works had been published concerning the effects of various factors on the rates of toluene alkylation by  $C_{10}$  olefins in the presence of sulfuric acid.

It was recently shown [8] that in the presence of phosphoric acid the process of amylene (a component of the  $C_8$  fraction among the products of thermal cracking) polymerization provides great possibilities as a source of high-molecular olefins, predominantly  $C_{10}$ , suitable for the manufacture of synthetic wetting agents. In connection with this, we conducted the present work for the purpose of studying toluene alkylation (in the presence of sulfuric acid) by the polymerization products of the pentaamylene fraction.

We used in these experiments toluene with a b. p. 109.5-111°,  $\rho_4^{20}$  0.8655,  $n_D^{20}$  1.4956, bromine number 0, and an amylene dimer fraction 125-175°, separated from a wide fraction of amylene polymers and possessing the following properties:  $\rho_4^{20}$  0.7663,  $n_D^{20}$  1.4354, M 134, and bromine number 120, which corresponded to 100% (by weight) of unsaturated hydrocarbons.

Chemically pure sulfuric acid was used as a catalyst.

Alkylation was carried out in a laboratory-made glass reactor consisting of a cylinder with a spherical bottom and 1 liter capacity, equipped with a glass stirrer, mercury seal, a thermometer, a reflux condenser, and a dropping funnel for the addition of sulfuric acid. The reactor was placed in a bath which was supplied with a thermometer and a stirrer for a vigorous mixing of the cooling liquid. We carried out the experiment by placing a mixture of toluene and olefin fraction (at a preassigned ratio) into the reactor and then added sulphuric acid with rapid stirring so as to ensure a constant temperature. The addition usually took 0.5 min. on account of a rapid removal of the heat of reaction. After the acid was added the reaction mixture was stirred for a fixed length of time, allowed to settle, and the hydrocarbon layer was separated from the acid; it was made alkaline with 5% aqueous sodium hydroxide, washed with distilled water, dried over calcium chloride, and fractionally distilled, yielding unreacted toluene, an olefin fraction, and the alkylated product (fraction above 175°). Later the alkylated product was fractionated at 10-15 mm on a laboratory-made column with 20 theoretical plates and separated into two fractions, 175-220° and 220-300° (the desired fraction), and a residue, above 300°.

We carried out numerous experiments to find out the effects of the following factors: concentration of original acid, time and temperature of reaction, molar ratio of olefins to toluene and acid to hydrocarbon, on the alkylation of toluene by amylene dimers (125-175° fractions).

When the initial concentration of the acid was changed from 80 to 100% (by weight of the monohydrate) at 10°, 60 min. reaction time, molar ratio of olefin to toluene 1:7, and a 0.12 ratio by volume of acid to hydrocarbons, the yield of alkylated products (fraction above 175°) changed from 9.1 to 125.5% (by weight of the original olefins) and had a maximum of 143 wt % at 96% acid strength.

TABLE 1

The Effect of Temperature on the Yield and Properties of Alkylated Products. Conditions: 96 wt. % initial acid concentration, 60 min reaction time, volume ratio of acid to hydrocarbons 0.12, molar ratio of olefins to toluene 1:7.

Experiment No.	Temperature °C	Yield of alkylated product, (wt. % based on the olefins).	Alkylated product (fraction above 175°)			Properties of fractions						
			$\rho_4^{20}$	$n_D^{20}$	Br. No.	Fractional composition, wt. %			175-220°C		220-300°C	
						175-220°	220-300°	Residue above 300°	$\rho_4^{20}$	$n_D^{20}$	$\rho_4^{20}$	$n_D^{20}$
26	-10	131.5	0.8730	1.4912	3.2	7.2	90.1	1.5	0.8615	1.4890	0.8718	1.4914
23	0	135.7	0.8719	1.4919	3.2	10.2	86.8	1.4	0.8645	1.4906	0.8719	1.4920
14	10	143.0	0.8730	1.4920	4.0	13.3	82.9	2.0	0.8666	1.4920	0.8746	1.4921
24	20	139.5	0.8739	1.4924	4.6	11.6	84.3	2.1	0.8658	1.4915	0.8744	1.4926
27	30	141.0	0.8762	1.4927	4.3	16.1	80.1	2.4	0.8658	1.4926	0.8748	1.4928
28	40	126.0	0.8837	1.4918	6.8	20.9	75.8	1.7	0.8658	1.4918	0.8846	1.4913

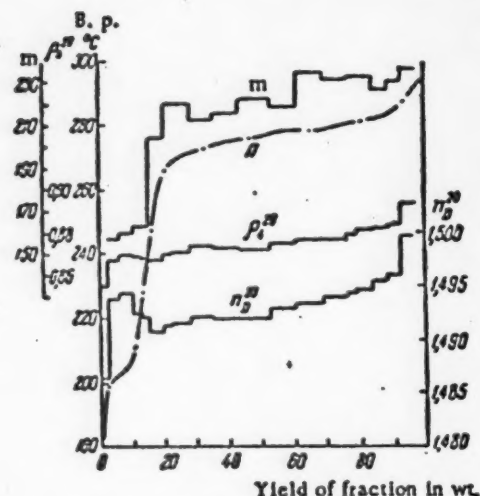


Fig. 1.

139.9% (by weight) at 1:4 molar ratio, then insignificantly. Moreover, the bromine number of the alkylated product decreased from 12.4 to 2.9.

We studied the effect of change in the acid to hydrocarbons volume ratios from 0.05 to 0.5 at 10°, 60 min reaction time, 96% acid concentration, and a molar ratio of olefins to toluene 1:7, and found out that the yield kept increasing only until a 0.12 ratio was attained, and after that remained practically unchanged.

The experiments we carried out enabled us to determine the following optimum conditions which guaranteed the maximum yield of alkylated product: initial acid concentration 95-97% by weight of monohydrate, temperature 10-15°, reaction time 30-40 min, molar ratio of olefins to toluene 1:4-1:6, volume ratio of acid to hydrocarbons 0.12.

Under these conditions the yield of alkylated product was 140-143% by weight of starting olefins.

It was previously considered [5-8] that during alkylation of benzene and toluene with butylene in the presence of sulfuric, hydrofluoric, and alkylsulfonic acids a considerable depolymerization of the original (dimeric) olefins took place with a subsequent alkylation of the aromatic hydrocarbon by the monomers. Our experiments

This change also lowered the bromine number of the alkylated product from 30.6 to 2.9.

As may be seen in Table 1, when temperature was raised from -10 to +40° the yield of alkylated product changed from 131.5 to 126% at 10-15°. Moreover, the bromine number increased with rise in temperature.

When the reaction time was changed from 0.5 min (length of time the acid was added excluding the additional stirring) to 90 min (addition time plus subsequent stirring) at 10°, 96% acid concentration, 1:7 molar ratio of olefin to toluene, and 0.12 acid to hydrocarbon ratio, it was found out that the formation of alkylated product was practically complete after 30 min, and that if the reaction time was increased above 60 min a slight decrease in the yield of alkylated product occurred.

When the molar ratio of olefins to toluene was changed from 1:0.5 to 1:10, the yield of alkylated product increased from 90.2 to 145.8% (by weight, based on the starting olefins) sharply at first, attaining



on the alkylation of toluene by amylene dimers in the presence of sulfuric acid indicated that depolymerization occurred to a lesser degree than was previously assumed. Under optimum conditions the 175-220° fraction (in which amyltoluenes are concentrated) did not exceed 12-13% (by weight) of the alkylated products.

Beside all this, the experiments showed that only the initial acid concentration and the reaction temperature had any appreciable effect on the yield of the amyltoluene fraction. When the acid concentration was decreased and the reaction temperature raised, the yield of amyltoluene fraction (175-220° fraction) in the alkylated products increased from 10.4 to 16.5 wt. %; as may be seen in Table 1, when the reaction temperature was changed in the -10 to +40° range, the yield increased from 7.2 to 20.9% (by weight) of alkylated products.

Under near-optimum conditions: 10°, 60 min reaction time, 1:7 molar ratio of olefins to toluene, 0.12 volume ratio of acid to hydrocarbons, we obtained alkylated products with the following properties. Unfractionated alkylated product:  $\rho_4^{20}$  0.8730;  $n_D^{20}$  1.4920; M 216; bromine number 4.0; aniline maximum point 15°. The 175-220° fraction of alkylated product:  $\rho_4^{20}$  0.8666;  $n_D^{20}$  1.4920; M 159.5. The 220-300° fraction of alkylated product:  $\rho_4^{20}$  0.8746;  $n_D^{20}$  1.4921; M 211. The residue above 300°:  $\rho_4^{20}$  0.9010;  $n_D^{20}$  1.4930. In Fig. 1 we have plotted the fractional distillation curve for alkylated product (p) and the characteristics of its narrow fractions.

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# RATE MECHANISM OF THE REACTION BETWEEN METHANE AND NITROGEN DIOXIDE

T. V. Fedorova, A. P. Ballod, Academician A. V. Topchiev, and V. Ia. Shtern

The works found in the literature on the vapor-phase nitration of alkanes by nitrogen dioxide are generally concerned with the synthesis itself, and the hypotheses proposed for the rate mechanism of this reaction are based on indirect evidence [1-9]. One can most probably reject a molecular mechanism in such a nitration in favor of one involving free radicals. However, it is not clear until now whether it is a simple free-radical reaction or a chain process. We devoted the present work to the solution of this problem by establishing the formal kinetic regularities in the reaction.

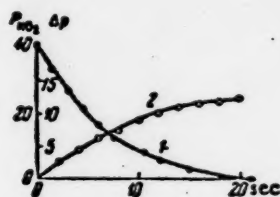


Fig. 1. Kinetic curves of  $\Delta p$  vs.  $(t)$  and  $P_{NO_2}$  vs.  $(t)$  for a mixture of  $4 CH_4 + 1 NO_2$  at  $T = 450^\circ$ .  $P_{initial} = 200$  mm. 1)  $P_{NO_2}$ ; 2)  $\Delta p$ .

Earlier [10] we have shown that, depending on the initial conditions, the nitration of methane by nitrogen dioxide took one of three courses for which the kinetic curves of pressure increment vs. time ( $\Delta p$  vs.  $(t)$ ) had different forms: a) slow reaction, b) reaction with a maximum on the  $\Delta p$  vs.  $(t)$  curve, c) combustion reaction. In the present communication we have reported experimental results obtained for the case of a slow reaction with a small degree of conversion. The shape of kinetic curves for  $\Delta p$  vs.  $(t)$  and  $P_{NO_2}$  vs.  $(t)$  in a slow reaction are shown in Fig. 1.

In order to determine the orders of reactions with respect to the starting materials, we studied the dependence of initial nitration rates on the concentration of one component when the other was kept constant.

The initial nitration rate was calculated from the amount of  $NO_2$  consumed in the reaction. Since dissociation of  $NO_2$  proceeds simultaneously with the reaction between  $NO_2$  and  $CH_4$ , the initial rates computed from the consumption of  $NO_2$  are a sum of the nitration and dissociation rates. Therefore, to determine strictly the initial nitration rate ( $W_{nitr}$ ) we subtracted the initial dissociation rate of  $NO_2$  ( $W_{diss}$ ) from the total initial rate of the over-all process. Since a dilution of the  $4 CH_4 + 1 NO_2$  mixture with nitrogen by a factor of 4.6 (from 100 to 450 mm of Hg at  $T = 450^\circ$ ) had no effect on the initial reaction rates, then within the limits of the above-mentioned dilution range there was no need to carry out the experiments at a constant initial pressure.

The order of reaction with respect to  $CH_4$  was determined at a constant initial  $P_{NO_2} = 40$  mm, for mixture varying in composition from  $1 CH_4 + 1 NO_2$  to  $12 CH_4 + 1 NO_2$ . The corresponding data are shown in Fig. 2. The order of reaction with respect to  $CH_4$ , as determined from the slope of the line obtained, was  $1 \pm 0.1$ , i. e., practically one.

To determine the order of reaction with respect to  $NO_2$ , we carried out three sets of experiments at  $T = 450^\circ$  with constant initial  $P_{CH_4}$  equal to 100, 153, and 200 mm of Hg. Moreover, utilizing the already known order with respect to  $CH_4$ , we transformed to  $P_{CH_4} = 200$  mm the results obtained in a series of experiments with initial  $P_{CH_4}$  equal to 100 and 153 mm of Hg. The data are shown in Fig. 3. After the data was processed by the method of least squares we obtained a linear equation:

$$\lg W_{nitr} = -1.12 + 1.1 \lg P_{NO_2}$$

whose slope gave the order of reaction with respect to  $\text{NO}_2$  as equal to 1.1. Thus, the order of reaction with respect to  $\text{NO}_2$  as well as to  $\text{CH}_4$  was practically equal to one.

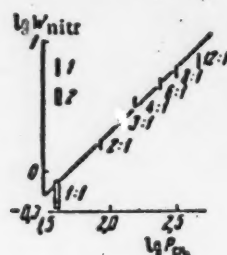


Fig. 2

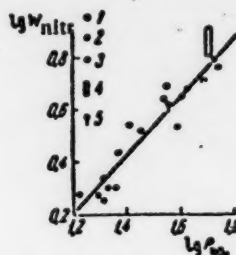


Fig. 3



Fig. 4

Fig. 2. Determination of the order of reaction between  $\text{CH}_4$  and  $\text{NO}_2$  with respect to  $\text{CH}_4$  at  $T = 450^\circ$  and  $P_{\text{NO}_2} = 40$  mm. 1) Mean square error in the determination of the logarithm of the rate of  $\text{NO}_2$  consumption; 2) mean square error in the determination of the logarithm of the rate of  $\text{NO}_2$  consumption plus the logarithm of  $\text{CH}_4$  concentration.

Fig. 3. Determination of the order of reaction between  $\text{CH}_4$  and  $\text{NO}_2$  with respect to  $\text{NO}_2$  at  $T = 450^\circ$ . The values of  $P_{\text{CH}_4}$  (in mm of Hg) are: 1) 200; 2) 153; 3) 100. Results of a series of experiments carried out at  $P_{\text{CH}_4}$  equal to 153 and 100 mm of Hg transformed to  $P_{\text{CH}_4} = 200$  mm; 4) mean square error in the determination of the logarithm of the rate of  $\text{NO}_2$  consumption plus the logarithm of  $\text{NO}_2$  concentration; 5) coinciding result of two measurements.

Fig. 4. Determination of the activation energy for the reaction between  $\text{CH}_4$  and  $\text{NO}_2$ . 4  $\text{CH}_4 + 1 \text{NO}_2$  mixture. 1) Results of a series of experiments carried out at  $P_{\text{in}} = 50$  mm; 2) transformed to  $P_{\text{in}} = 100$  mm; 3) mean square error in the determination of the logarithm of the rate of  $\text{NO}_2$  consumption; 4) a coinciding result of two measurements.

TABLE 1

Determination of The Activation Energy for The Reaction Between Methane and Nitrogen Dioxide by The Method of Comparing The Methane Nitration and Nitrogen Dioxide Dissociation Rates,  $E_{\text{diss}} = 26.9$  kcal/mole,  $f_{\text{diss}} = 0.06$ ;  $f_{\text{nitr}} = 1.0$ .

Expt. No.	T, °C	CH <sub>3</sub> :NO <sub>2</sub>	P <sub>in</sub>	P <sub>CH<sub>4</sub></sub>	P <sub>NO<sub>2</sub></sub>	W <sub>nitr</sub>	W <sub>diss</sub>	E, kcal/mole
			mm of Hg			mm of Hg		
325	450	1:1	78,5	39,25	39,25	0,67	1,14	29,5 ± 2,5
450	450	6:1	239	200	39	3,42	1,14	29,5 ± 2,5
17	500	2:1	52,5	35	17,5	4,0	0,8	28,4 ± 1,4
193	500	4:1	103,5	82,8	20,7	3,44	1,1	29,4 ± 2,4
508	440	4:1	100	80	20	0,68	0,22	29,2 ± 2,2
315	450	4:1	121,4	97,8	23,6	1,08	0,42	29,6 ± 2,6

Activation energy for the reaction between  $\text{CH}_4$  and  $\text{NO}_2$  was determined graphically from the Arrhenius Equation for a 4  $\text{CH}_4 + 1 \text{NO}_2$  mixture in the 400-500° temperature range and with  $P_{\text{in}} = 50$  and 100 mm of Hg. Results of a series of experiments carried out at  $P_{\text{in}} = 50$  mm were transformed to  $P_{\text{in}} = 100$  mm; this, of course, could now be done, since the orders of reactions were already known. The initial nitration rates were determined, as was mentioned before, from the difference between the total initial rate of  $\text{NO}_2$  consumption and the initial  $\text{NO}_2$  dissociation rate. The data for the determination of  $E_{\text{nitr}}$  are shown in Fig. 4. The line corresponds to the equation derived by the method of least squares,

$$\lg W_{\text{nitr}} = 9.2 - 6.5 \frac{1}{T} \cdot 10^3.$$

The slope gives a value of  $E_{\text{nitr}} = 30.5$  kcal/mole.

In our case, where we studied a process consisting of two concurrent reactions (nitration of the hydrocarbon and dissociation of  $\text{NO}_2$ ), we were able to determine the value of  $E_{\text{nitr}}$  by another independent method, namely, by comparing the rates of these two reactions.

Let us write the rate equations for these two reactions at the same temperature and  $\text{NO}_2$  concentration,

$$W_{\text{nitr}} = f_{\text{nitr}} Z e^{-E_{\text{nitr}}/RT} [\text{CH}_4] [\text{NO}_2], \quad (I)$$

$$W_{\text{diss}} = f_{\text{diss}} Z e^{-E_{\text{diss}}/RT} [\text{NO}_2]^2, \quad (II)$$

where  $Z$  = collision number,  $f$  = steric factor. Let us divide Equation (I) by Equation (II) and take the logarithm of the quotient.

$$E_{\text{nitr}} = (\lg \frac{f_{\text{nitr}}}{f_{\text{diss}}} + \lg \frac{[\text{CH}_4]}{[\text{NO}_2]} - \lg \frac{W_{\text{nitr}}}{W_{\text{diss}}}) \frac{RT}{0.43} + E_{\text{diss}}. \quad (III)$$

According to the data [11]  $E_{\text{diss}} = 26.9$  kcal/mole,  $f_{\text{diss}} = 0.66$ ; according to the data [12]  $E_{\text{diss}} = 27.1$  kcal/mole, and according to our data  $E_{\text{diss}} = 27$  kcal/mole. The steric factor in the nitration ( $f_{\text{nitr}}$ ) is not known. In general, it varies from  $10^{-4}$  to 1 in bimolecular reactions.

If we use the extreme values of  $f_{\text{nitr}}$  we get: for  $f_{\text{nitr}} = 10^{-4}$ ,  $E_{\text{nitr}} = 18.4$  kcal/mole, while for  $f_{\text{nitr}} = 1$ ,  $E_{\text{nitr}} = 31.9$  kcal/mole (for initial conditions see Table 1, Expt. No. 325). It is possible, however, to narrow down the range of  $E_{\text{nitr}}$  values. The ratio  $W_{\text{nitr}}/W_{\text{diss}}$  increases with increase in temperature. Thus, for the composition  $4 \text{CH}_4 + 1 \text{NO}_2$  at  $P_{\text{in}} = 50$  mm and  $400^\circ$ ,  $W_{\text{nitr}}/W_{\text{diss}} = 3$ , while at  $500^\circ$   $W_{\text{nitr}}/W_{\text{diss}} = 12.5$ . Consequently, the value of  $E_{\text{nitr}}$  should be larger than  $E_{\text{diss}}$ , i. e.,  $E_{\text{nitr}}$  has to be in the range of 27-32 kcal/mole. Table 1 lists the data from the determination of  $E_{\text{nitr}}$  by the comparison of  $\text{CH}_4$  nitration and  $\text{NO}_2$  dissociation rates at various temperatures and compositions.

After comparing the values of  $E_{\text{nitr}}$  determined by the Arrhenius Equation with the ones determined from the ratio of two concurrent reaction rates, we settled for the value  $E_{\text{nitr}} = 30$  kcal/mole.

Having chosen a value for  $E_{\text{nitr}}$  it was then possible to estimate  $f_{\text{nitr}}$  by substituting experimentally determined rates in Equation (I). The steric factor in the nitration of methane by  $\text{NO}_2$  turned out to be 0.5.

Experiments were also designed for the purpose of determining whether the nitration of methane was a homogeneous or heterogeneous reaction. Replacement of a quartz reactor by one made of molybdenum, aging of reactor, changing the S/V ratio from 0.97 to 20.0, and coating the reactor walls with KCl did not have any noticeable effect on the reaction rates. From this we could conclude that the reaction was homogeneous.

The above-described kinetic investigation of the vapor-phase nitration of  $\text{CH}_4$  by nitrogen dioxide led to the following expression for the rate of this reaction,

$$W_{\text{nitr}} = 0.5 \cdot 10^{-19} e^{-30000/RT} \cdot (\text{CH}_4) (\text{NO}_2) \text{ liter}^{-1} \cdot \text{sec}^{-1}.$$

A question arose as to whether the measured reaction rate was determined by the slowest bimolecular step in a free-radical reaction or whether it was the rate of a complex chain reaction which behaved like a bimolecular reaction. A series of authors [3, 4] have proposed the following initiating step in the nitration,



Currently there have appeared in the literature data proving the existence of  $\text{HNO}_2$  in the gas phase [13] as well as values for the heat of formation of gaseous  $\text{HNO}_2$  [14, 15]. The latter make it possible to calculate the thermodynamic Heat of Reaction (I) (for methane) and to make an approximation to the activation energy, assuming that the empirical formula of Semenov-Polanyi [16] for an endothermic free-radical reaction is applicable. For  $\Delta H_{\text{HNO}_2} = -13.7$  kcal/mole [14]  $E_{\text{nitr}} = 32.7$  kcal/mole, and for  $\Delta H_{\text{HNO}_2} = -20$  kcal/mole [15],  $E_{\text{nitr}} = 27.9$  kcal/mole.

Thus, the activation energies calculated for Equation (I) are close to the ones determined in this work from experimental data.

It is also striking that in the nitration we obtained first order rates with respect to  $\text{CH}_4$  and  $\text{NO}_2$ , i. e., the same dependence on initial concentration as in Equation (1).

All this leads us to the conclusion that the kinetics we obtained for the nitration of methane were determined by Reaction (1), which was therefore the rate-determining step in the whole reaction.

Additional support for this conclusion came from the results obtained in our laboratory by I. V. Patsevich, who showed that the activation energies of the two routes which the reaction between alkyl radicals and  $\text{NO}_2$  could take,  $\text{RNO}_2 \xrightarrow{a} \text{R} + \text{NO}_2 \xrightarrow{b} \text{RONO}$  differed by  $\sim 1$  kcal/mole, while the steric factor was 0.6. Consequently, at  $450^\circ$  the rate ratio  $W_a/W_b = 0.6e^{1000/2.723} = 1.2$ .

Since each time  $\text{RNO}_2$  is formed it constitutes a chain termination, then the maximum chain length in the nitration reaction can not exceed two members. With such rate ratio between reactions (a) and (b) the nitration cannot be considered a complex chain reaction which behaves like a bimolecular reaction.

As a result, the mechanism of methane nitration (if we can disregard secondary reactions of intermediate compounds) boils down to the following. The slow initiating step in which alkyl radicals are formed as in Equation (1) ( $E_{\text{nitr}} = 30$  kcal/mole,  $f_{\text{nitr}} = 0.5$ ) is followed by a reaction between these radicals and  $\text{NO}_2$ ; this reaction evidently has a small activation energy and proceeds by route (a) or (b), since  $\text{NO}_2$  is a radical-like molecule. Therefore, it can be assumed that the calculated activation energy, 30 kcal/mole is the energy of the initiating step.

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\*Original Russian pagination. See C. B. Translation.

\*\*In Russian.



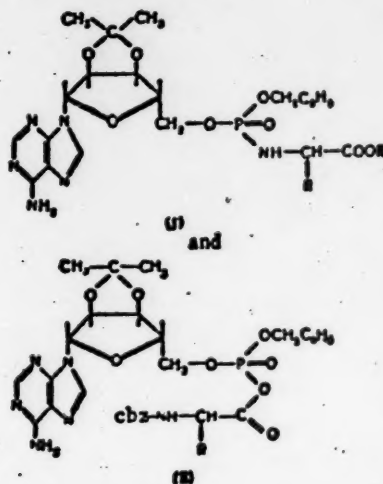
## SYNTHESIS OF p-AMINO ACID DERIVATIVES OF ADENILIC ACID

Z. A. Shabarova, L. G. Satarova, and M. A. Prokof'ev

(Presented by Academician A. N. Nesmelanov July 16, 1958)

It is known that amino acid and peptide derivatives of nucleic acids and nucleotides play an important part in a series of biochemical processes, including the directed synthesis of albumin. However, the chemistry of these compounds is still in an early stage of development. Of the various types of amino acid and peptide derivatives the compounds in which amino acids are linked to the mononucleotides through a phosphate radical have a particular function in biochemical processes. Hence, the synthesis and study of properties of such compounds were the primary objectives of this work.

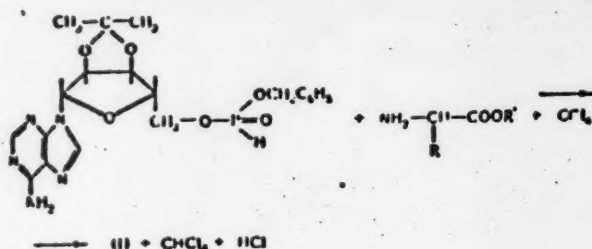
We synthesized two types of amino acid derivatives of adenosine-5'-phosphate:



Compounds of type (I), containing a phosphoamino linkage between the nucleotide and amino acid, have not been described in the literature, although the existence of such a linkage between the nucleotide and amino acids in living organisms had already been discussed [1].

We synthesized these compounds from 2':3'-isopropylideneadenosine-5'-benzylphosphite (III) [2] by treating it with an ester of amino acid in the presence of  $\text{CCl}_4$ .

\* We used the method of amine phosphorylation developed by Todd and co-workers [3] which consisted of a reaction between esters of phosphoric acid and primary amines in the presence of  $\text{CCl}_4$ .



The physical constants and yields of the synthesized esters of N-adenylamino acids are listed in Table 1:

According to the literature data [4], the P - N bond in compounds of type (I) have a characteristic I.R. frequency, 11.38-11.60 $\mu$ . The esters of N-adenylamino acids synthesized by us also had a characteristic frequency in the 11.48-11.59 $\mu$  region (see Table 1).

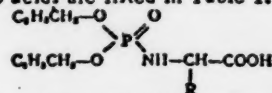


TABLE 1

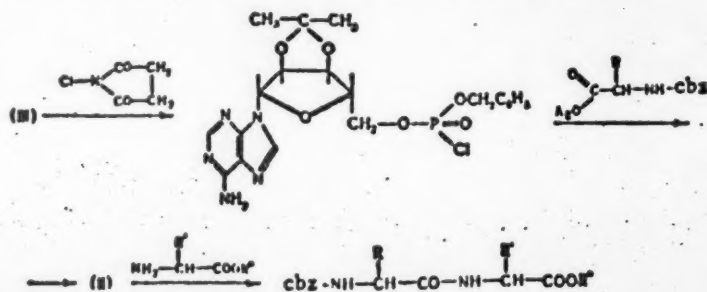
Name of Compound	Yield, %	M. p. (with decompn.), °C	U. V. absorption		Characteristic I. R., $\mu$
			$\lambda_{\text{max}}$ , m $\mu$	$\epsilon$	
Ethyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-phenylalanine	62,5	88 - 90	260	13250	11,59
Methyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-glycine	52	60 - 63	260	11500	11,48
Methyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-leucine	44	68 - 72	260	9800	11,56

The proposed method of synthesizing esters of N-adenylamino acids is simple to carry out and ensures sufficiently high yields; therefore, it can be considered a good general preparatory method and can, obviously, be extended to other nucleotides.

To study the stability of the P - N bond in the synthesized compounds, and also to obtain additional structure proof for compounds of type (I), we hydrolyzed them with alkali and acids. We found out that the P - N bond in compound (I) is readily hydrolyzed by acids (0.1N, 30 min, 100°), less readily by alkali (2N, 30 min, 100°). Chromatographic analysis of hydrolysis products showed the presence of amino acids and of nucleotide decomposition products.

Methods of synthesizing mixed anhydrides of adenilic and amino acids have in recent years been very intensively investigated. It was established that mixed anhydrides formed when adenilic acid or its salts reacted with acyl chlorides of amino acids [5], thiophenyl esters of amino acids [6], mixed anhydrides of amino acids and carbonic acid monoesters [7],  $\alpha$ -azidoacids [8].

We succeeded in synthesizing mixed anhydrides of adenilic acid with cbz-leucine\* and cbz-glycine from 2':3'-isopropylideneadenosine-5'-benzylphosphite according to the following scheme:



\*Carbobenzyloxy-N-leucine.

Since we were interested in finding out how readily would compound (II) react with amino acids to form peptides, we did not isolate the compound but allowed it to react with the amino acid ester. In this way we prepared mixed anhydrides of 2':3'-isopropylideneadenosine-5'-benzylphosphoric acid with cbz-glycine (IIa) and cbz-leucine (IIb). Compounds (IIa) and (IIb) reacted with methyl esters of phenylalanine and glycine, respectively, to form the esters of cbz-glycylphenylalanine and cbz-leucylalanine. The formation of dipeptides was established chromatographically.

## EXPERIMENTAL

### Ethyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-phenylalanine (Ia).

To a solution of 0.08 g of dry 2':3'-isopropylideneadenosine-5'-benzylphospho-phenylalanine (Ia) [2] in 5 ml of absolute  $\text{CCl}_4$  we added 0.1 g of freshly prepared ethyl ester of phenylalanine in 2 ml of absolute  $\text{CCl}_4$ . The reaction mixture was left overnight, then evaporated in vacuo, and the residual oil dissolved in chloroform. The chloroform solution was washed with water, 0.1N HCl, conc.  $\text{NaHCO}_3$ , and with water again. After drying the solution over  $\text{MgSO}_4$  we evaporated the chloroform in vacuo and dissolved the oil in 1 ml of benzene. The benzene solution was poured with stirring into dry petroleum ether (40-60° fraction). The precipitate was separated by decantation. The compound was purified by two-fold reprecipitation and dried in vacuo (5 mm) over  $\text{P}_2\text{O}_5$  at 37°. The yield of compound (Ia) was 0.069 g (62.5%). M. p. 88-90° (with decompn.).

$R_f = 0.91$  in a n-butanol + water + acetic acid (5:3:2) system (system I).

$R_f = 0.93$  in a system of n-butanol saturated with water (system II).

Found %: C 53.45; H 5.96; N 11.76; P 4.20  $\text{C}_{31}\text{H}_{37}\text{O}_8\text{N}_4\text{P} \cdot 3\text{H}_2\text{O}$ . Calculated %: C 53.14; H 6.14; N 11.90; P 4.30.

U. V. absorption (in 95%  $\text{C}_2\text{H}_5\text{OH}$ ):  $\lambda_{\text{max}} = 259-260\text{m}\mu$  (13,250). Characteristic I. R. frequency = 11.59  $\mu$ .

Acid hydrolysis of compound (Ia). A solution of 5 mg of compound (Ia) in 2 ml of 0.1N  $\text{H}_2\text{SO}_4$  was refluxed for several hours. At fixed time intervals samples of the hydrolyzed product were analyzed chromatographically on an ascending column in system (I). After 30 min, chromatography indicated that the starting material (Ia) disappeared from the hydrolyzed mixture while phenylalanine ( $R_f = 0.72$ ) and a compound with  $R_f = 0.47$  and absorbing in U. V.\* appeared. The aqueous-alcoholic eluted fraction of the  $R_f = 0.47$  spot had a U. V. absorption maximum at 258-260  $\text{m}\mu$ .

Alkaline hydrolysis of compound (Ia). The P-N bond in compound (Ia) was not hydrolyzed when refluxed for two hours in 0.1N NaOH. The chromatogram showed only the starting materials. When compound (Ia) was refluxed for 30 min in 2N NaOH, phenylalanine was cleaved and detected chromatographically ( $R_f = 0.72$  in system I).

### The methyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-glycine (Ib).

Compound (Ib) was prepared from compound (III) and methyl ester of glycine by the same method as compound (Ia). The yield of compound (Ib) was 52%, m. p. 60-63° (with decompn.).  $R_f = 0.91$  in system (I).

Found %: N 13.62; P 4.76.  $\text{C}_{23}\text{H}_{29}\text{O}_8\text{N}_4\text{P} \cdot 3\text{H}_2\text{O}$ . Calculated %: N 13.95; P 5.14.

U. V. absorption (in 96%  $\text{C}_2\text{H}_5\text{OH}$ ):  $\lambda_{\text{max}} = 260\text{m}\mu$  ( $\epsilon = 11,500$ ). Characteristic I. R. frequency 11.48  $\mu$ .

Acid (0.1N  $\text{H}_2\text{SO}_4$ ) and alkaline (2N NaOH) hydrolysis of compound (Ib) proceeded similarly to that of compound (Ia).

Glycine ( $R_f = 0.37$  in system I) was detected chromatographically among the hydrolysis products.

### Methyl ester of N-(2':3'-isopropylideneadenosine-5'-benzylphospho)-leucine (Ic).

It was synthesized from compound (III) and the methyl ester of leucine in the same way as compound (Ia). The yield of (Ic) was 44%. M. p. 68-72° (with decompn.).  $R_f = 0.93$  in system (I).

Found %: N 12.2; P 4.3.  $\text{C}_{31}\text{H}_{37}\text{O}_8\text{N}_4\text{P} \cdot 3\text{H}_2\text{O}$ . Calculated %: N 12.8; P 4.7.

\* Detected when the chromatogram was scanned in a Broomberg Chemoscope.

Alkaline (2N NaOH) and acid (0.1N H<sub>2</sub>SO<sub>4</sub>) hydrolysis of compound (Ic) splits out the amino acid just as in compounds (Ia) and (Ib). Leucine was detected chromatographically ( $R_f = 0.73$  in system (I)).

Mixed anhydride of 2':3'-isopropylideneadenosine-5'-benzylphosphoric acid and cbz-leucine (IIa).

We added 0.10 g of N-chlorosuccinimide to 0.2 g of compound (III) dissolved in 5 ml of absolute benzene and 3 ml of absolute CH<sub>3</sub>CN [9]. After 2 hours the solution was filtered. We added to the filtrate 0.07 g of dry silver salt of cbz-leucine [10] dissolved in 5 ml of absolute dioxane. The mixture was left overnight. The residue was filtered out, and evaporated in vacuo. The oil was triturated in absolute ether. To the ether extract (IIa) we added 0.1 g of methyl ester of glycine. The solution was left for 24 hours, evaporated, and separated chromatographically in a system of n-butanol saturated with ammonia (system (III)). After being dried the chromatogram was developed in benzidine. A spot with  $R_f = 0.93$  was detected; methyl ester of cbz-leucylglycine when placed on the chromatogram as a control also had  $R_f = 0.93$ .

A mixed anhydride of 2':3'-isopropylideneadenosine-5'-benzylphosphoric acid and cbz-glycine.

It was similarly prepared from compound (III) and Ag salt of cbz-glycine.

The anhydride was extracted with ether and allowed to react with the methyl ester of phenylalanine. We chromatographically detected the methyl ester of cbz-glycylphenylalanine ( $R_f = 0.67$  in system (III)).

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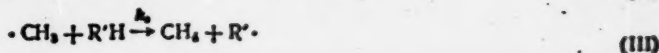
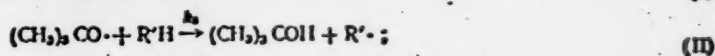
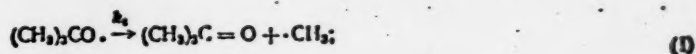
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## REACTIONS OF OXIDE RADICALS OF TYPE RO·

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S. S. Medvedev

The oxidation of hydrocarbons, in particular carbon-chain polymers, proceeds through the formation of hydrogen peroxide compounds which decompose under the conditions of the reaction to form radicals of type RO·; it was interesting, therefore, in connection with this to study reactions in which these radicals participate. These reactions were chiefly investigated by the use of model systems in which RO· radicals were formed by decomposition of dialkyl peroxides. We found out, that when di-tert-butyl peroxide decomposed in hydrocarbon solvents the main reaction products were acetone, tert-butyl alcohol, and methane; the following scheme was proposed to account for the formation of these.



According to this scheme, the ratio between the concentration of acetone  $a$  and tert-butyl alcohol  $b$ ,  $a/b = k_1/k_2 - 1/[\text{R}'\text{H}]$  (where  $\text{R}'\text{H}$  = solvent concentration). With the help of this equation and by using data on the formation of acetone and tert-butyl alcohol at 135°, Brooks calculated [1, 2] the values of  $k_1/k_2 - 1/[\text{R}'\text{H}]$  for the reactions of tert-butoxy radicals in various solvents. The values he found were in the range from 0.05 to 0.5, which indicated that reaction (I) proceeded at an appreciable rate. One would think that in the case of polymers the reaction would lead to a rupture of C-C bonds in the polymeric molecules, and that consequently to a lowering of the molecular weight. The activation energy  $E_1 - E_2 \approx 8$  kcal/mole determined in that same work indicated that at higher temperatures the role of this reaction would increase.

Investigation of the di-tert-butyl peroxide decomposition products at 195° showed [3] that at that temperature the yield of acetone exceeded that of tert-butyl alcohol by a factor of 12, which indicated a higher activation energy than that found by Brooks.

If we start from the scheme shown above, then the data obtained indicate that at these temperatures almost all the decomposition of tert-butoxy radicals is accompanied by a rupture of C-C bonds; this conflicts with the data found in the literature on the thermal decomposition + oxidation of carbon-chain polymers [4].

The above-listed data provide a basis for the assumption that the formation of acetone during decomposition of di-tert-butylperoxide results not only from reaction (I), but also from some other kind of a reaction whose rate strongly depends on temperature. One such reaction could be that of RO· radicals with each other. At lower temperatures, when the concentration of RO· radicals is low, the rate of this reaction, as Brooks' data indicated, is comparatively slow. When, however, the temperature is raised (or when peroxide concentration is considerably increased) the concentration of RO· radicals in the system, and consequently the rate of this reaction will sharply increase; this will in turn result in higher yields of acetone as compared to the yield of tert-butyl alcohol.

In order to verify this assumption, we investigated the decomposition of di-tert-butyl peroxide at 120-150° in isopropylbenzene solution over the 4-16 wt. % concentration range. The concentrations of reaction products were determined by the use of infrared spectra: acetone by the 1714  $\text{cm}^{-1}$  absorption band tert-butyl alcohol



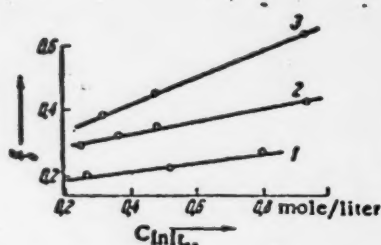


Fig. 1. The dependence of acetone:tert-butyl alcohol molar ratio on the initial concentration of peroxide. 1) 120°; 2) 135°; 3) 150°.

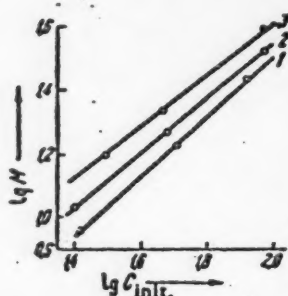


Fig. 2. Determination of  $\alpha$ . 1) 120°; 2) 135°; 3) 150°.

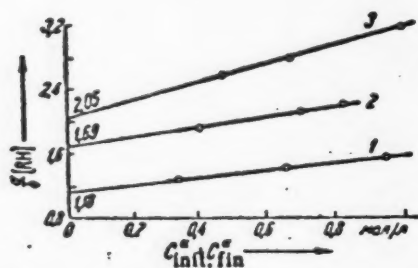
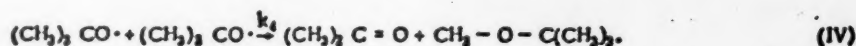


Fig. 3. Determination of the ratio of rate constants,  $k_1/k_2$ . 1) At 120°; 2) at 135°; 3) 150°.

( $C_{init}$ ) the larger the difference between their yields.

The formation of acetone in the reaction between two  $RO\cdot$  radicals can be described by the following scheme,



In this case the total rate of acetone formation is

$$\frac{da}{dt} = k_1[RO\cdot] + k_2[RO\cdot]^2 \quad (I)$$

TABLE 1

The Quantity of Acetone and Methane Formed During Decomposition of Peroxide at 135°

$C_{init}$ , moles/liter	$a$ , moles/liter	$m$ , moles/liter	$m/a$
0,268	0,101	0,0846	0,838
0,356	0,130	0,1035	0,796
0,818	0,352	0,264	0,75

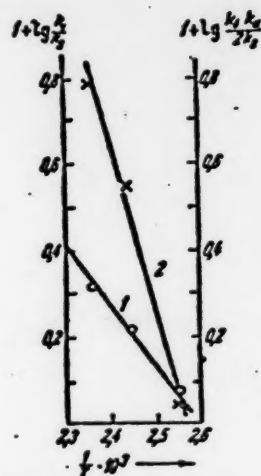


Fig. 4. Determination of activation energy. 1)  $k_1/k_2$  2)  $k_2 k_1 / 2k_2$

by absorption in the  $3000\text{ cm}^{-1}$  region, peroxide in the  $878\text{ cm}^{-1}$  region (also iodometrically); methane was determined volumetrically.

The data given in Fig. 1 show that the value of  $a/b$  ratio increases with increase in peroxide concentration. This indicates that the formation of these compounds is not a first-order reaction with respect to peroxide concentration. Besides, as may be seen in Table 1, the yield of methane is lower than that of acetone, and the higher the peroxide concentration

The rate of peroxide decomposition is

$$\frac{dC}{dt} = -k_c DC. \quad (2)$$

Dividing (1) by (2) we will get

$$\frac{da}{dC} = -\frac{k_1}{k_c} \frac{[RO\cdot]}{C} + \frac{k_4}{k_c} \frac{[RO\cdot]^2}{C}. \quad (3)$$

The concentration of RO· radicals in the system will depend on the conditions of stationary state

$$k_c C = k_1 [RO\cdot] + k_4 [RO\cdot]^2 + k_3 [RO\cdot] [R'\cdot]. \quad (4)$$

The concentration of RO· can be approximately expressed by equation

$$[RO\cdot] = k_\alpha C^\alpha. \quad (5)$$

where the number  $\alpha$  depends on the ratio between the rate constants of the first and second-order rupture (with respect to RO· radicals) and also on the concentration of RO· radicals. Substituting Equation (5) in (3), we obtain

$$\frac{da}{dC} = -\frac{k_1 k_\alpha}{k_c} C^{\alpha-1} - \frac{k_4 k_\alpha^2}{k_c} C^{2\alpha-1}. \quad (6)$$

Integrating this equation from  $a = 0, C = C_{init}$  to  $a, C = C_{fin}$  we get

$$a = \frac{k_1 k_\alpha}{k_c} (C_{init}^\alpha - C_{fin}^\alpha) + \frac{k_4 k_\alpha^2}{k_c \cdot 2\alpha} (C_{init}^{2\alpha} - C_{fin}^{2\alpha}). \quad (7)$$

The bulk of reaction products is formed before the concentration of radicals in the system undergoes any appreciable change. Therefore,  $\alpha$  can be assumed to remain constant during the whole reaction, and it can be calculated from the data on the formation of methane during peroxide decomposition:

$$\frac{dM}{dt} = k_1 [RO\cdot]. \quad (8)$$

Dividing Equation (8) by (2) and taking Equation (5) into account, we get

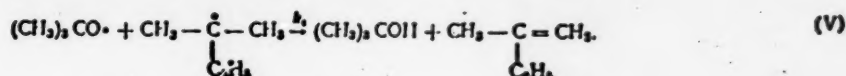
$$\frac{dM}{dC} = -\frac{k_1 k_\alpha}{k_c} C^{\alpha-1}. \quad (9)$$

Integrating this equation from  $M = 0, C = C_{init}$  to  $M = M, C = 0$ , and taking the logarithm of the resulting expression, we get

$$\lg M = \lg \frac{k_1 k_\alpha}{k_c} + \alpha \lg C_{init} \quad (10)$$

It may be seen in Fig. 2 that the experimental points fall satisfactorily on the lines expressed by this equation. The slopes of these lines correspond to the following values of  $\alpha$ : at  $120^\circ \alpha = 0.94$ ; at  $135^\circ \alpha = 0.86$ ; at  $150^\circ \alpha = 0.81$ . As one would expect, with increase in temperature the second-order rupture rate assumes a more important role.

In principle, alcohol could also be formed by a second-order reaction with respect to concentrations of RO· and R'· radicals.



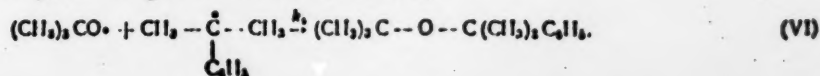
In this case

$$\frac{db}{dt} = k_2 [RO\cdot] [R'H] + k_3 [RO\cdot] [R'\cdot]. \quad (11)$$

Noting that  $[R'] = (n - [RO\cdot]) = kC^{1/2} - k_\alpha C^\alpha$ , where  $n$  = total concentration of free radicals, we can similarly get

$$\frac{b}{M} = \frac{k_2}{k_1} [R'H] + \frac{k_3 k_\alpha}{k_1 (\alpha + 1/2)} \frac{C_{init}^{\alpha+1/2} - C_{fin}^{\alpha+1/2}}{C_{init}^\alpha - C_{fin}^\alpha} - \frac{k_3 k_\alpha}{2k_1} (C_{init}^\alpha + C_{fin}^\alpha). \quad (12)$$

If the experimental data, however, are plotted with  $b/M$  as a function of  $C$ , a straight line parallel to the abscissa is obtained. This indicates that alcohol is formed only by a first-order reaction. The reaction between RO· and R'· radicals, obviously, will not give an alcohol, but an ether,



Thus, the equation involving  $b$  can be written in the following form.

$$b = \frac{k_2 k_\alpha}{k_c \alpha} [R^*H] (C_{init}^\alpha - C_{fin}^\alpha). \quad (13)$$

Dividing Equation (7) by (13), we will get

$$\frac{a}{b} = \frac{k_1}{k_2} \frac{1}{[R^*H]} + \frac{k_4 k_\alpha}{2k_2 [R^*H]} (C_{init}^\alpha + C_{fin}^\alpha). \quad (14)$$

By plotting the experimental data with  $\frac{a}{b} [R^*H]$  as a function of  $(C_{init}^\alpha + C_{fin}^\alpha)$  we will get straight lines whose slopes will be  $k_4 k_\alpha / 2k_2$ , and whose intercepts on the ordinate will be  $k_1 / k_2$  (Fig. 3).

Activation energy  $E_1 - E_2$  equals 7 kcal/mole, but for processes which are characterized by the expression  $k_4 k_\alpha / k_2$  and represent second order (with respect to concentration of  $RO^\bullet$  radicals) reactions leading to the formation of acetone; the activation energy is  $\sim 17.5$  kcal/mole (Fig. 4).

Consequently, the formation of acetone during decomposition of di-tert-butyl peroxide in hydrocarbon solvents at temperatures of the order of  $200^\circ$  is to a large extent connected with the bimolecular reaction (IV) and not with the monomolecular decomposition of  $RO^\bullet$  radicals.

In the case of high polymers, reaction (IV) should cause a pronounced change in the molecular-weight distribution; this actually takes place in highly oxidized polyethylene, where the change is accompanied by the appearance of ether bridges between macromolecules [5].

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\* See forthcoming C. B. Translation.

## USE OF BOILING POINT MEASUREMENTS IN THE PHYSICOCHEMICAL ANALYSIS OF BINARY LIQUID SYSTEMS

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(Presented by Academician B. A. Arbuzov June 12, 1958)

One of the properties of a liquid - vapor equilibrium is the boiling point. It may be used to characterize the compositions of liquid systems in the same manner as melting point is used to characterize the compositions in solid phase. Successful application of solid state thermal analysis, as well as results of vapor pressure studies on solutions indicate that boiling point measurements can also be used in physicochemical analysis [1, 2].

At the present time there is a large number of systems which have been investigated through the study of their boiling points; moreover, the most detailed studies were carried out on systems with no chemical affinity but possessing one associated component [3]. Irrational systems, which number about 300 [13, 10], and ideal systems have been studied in less detail. However, a large part of these investigations were carried out in search of azeotropes, frequently without a complete investigation of the boiling points of systems. Rational systems have not so far been studied ebulliometrically, with the exception of  $P_2O_5 - H_2O$ , which was not completely investigated either [4].

The experimental material, its classification and theoretical treatment in the literature are inadequate proof for the uses of boiling point measurements in physicochemical analysis. For this it is necessary to investigate the effects of chemical affinity between components on the boiling points of their systems. In other words, it is necessary to carry out a series of typical rational, then irrational systems, having established beforehand the forms of boiling point isobars of ideal and associated systems.

It is known that the vapor pressure of an ideal system is linearly dependent on the molal composition (Raoult's law). Consequently, the boiling point curve of an ideal system is slightly convex to the composition axis. Curves of this type are found in the literature. However, a shallow minimum is possible on the isobar if the boiling points of components are sufficiently close [5].

A boiling point curve of associated systems which exhibit a positive deviation from Raoult's law is convex towards the concentration axis of the graph and is located below the ideal boiling point isobar.

To complete the data of other authors we investigated two such systems: dioxane - ethylene glycol and nitrobenzene - isobutyl alcohol. Their boiling point isobars are of the same type and exhibit a considerable negative deviation from the ideal curve. This is connected with the fact that the molecules of the associated component dissociate in solution.

Determinations of the boiling point and vapor composition were carried out in an ebulliometer, which was a slightly modified form of V. A. Kireev's [6] and Sventoslavskii's [7] instruments. An electromagnetically regulated manostat was used to maintain a constant pressure in the apparatus. Temperature was measured on calibrated mercury thermometers; the composition of the condensate was determined refractometrically and in isolated cases by measuring other physical properties of the condensate.

Boiling point isobars of rational systems may exhibit three types of singular points: upper, middle, and lower.

We investigated six rational systems and obtained two types of boiling point isobars (with upper, and

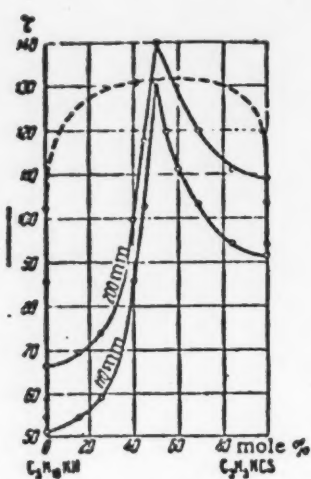


Fig. 1.

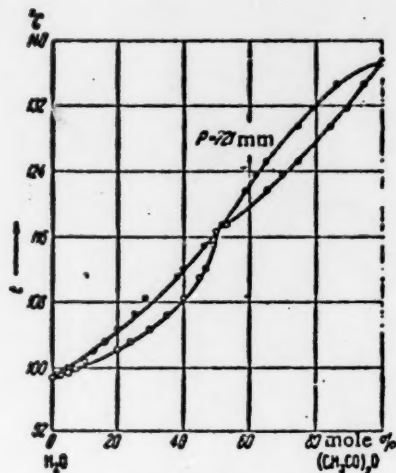


Fig. 2.

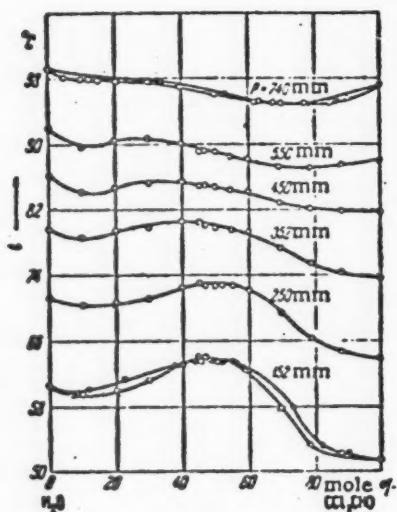


Fig. 3.

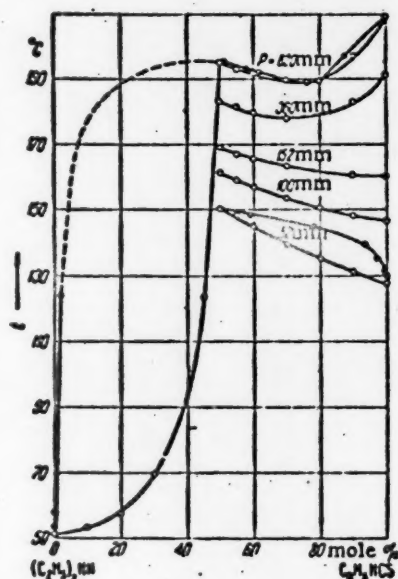


Fig. 4.

middle singular points). The most characteristic curves of the first type were obtained for the piperidine - allylisothiocyanate and ethylenediamine - allylisothiocyanate.

Boiling point curves of the first one (Fig. 1) consisted of two branches convex towards the composition axis and intersecting at a singular point which corresponded to a 1:1 component ratio. The latter circumstance indicates a formation of an undissociated compound  $C_3H_7NHSC_3H_5N$  which was also detected in the curves of other properties [1]. On the vapor composition curve the singular point corresponding to the compound does not show up too accurately. A similarly shaped condensation curve, where the branches creep at first alongside the ordinate and then, changing direction, meet at an obtuse angle, can be explained by the fact that the compound formed has a much higher heat of vaporization and boiling point than the components.



The boiling point isobar of the  $C_3H_5NCS - C_2H_5(NH_2)_2$  system did not essentially differ from the one previously described and had a singular point at 66.7 mole% of  $C_3H_5NCS$ . This indicated a formation of an undissociated compound  $(C_3H_5NHCSNH_2)_2C_2H_4$ , which conformed with the data on other properties of the system [8].

Boiling point isobars with a middle singular point at 50 mole% (ordinate value) are exhibited by water - acetic anhydride and diphenylamine - maleic anhydride systems.

The condensation curve of the water - acetic anhydride system (Fig. 2) consists of two branches with different signs of curvature intersecting, same as the vaporization curve, at a singular point, which indicates that the vapor contains some undissociated compound (acetic acid).

We were unable to detect experimentally any boiling point isobars with a lower singular point, and there is no mention of these in the literature. However, using the Method of Models [9], one can conclude that this type of a boiling point isobar is geometrically possible.

Alongside singular points one can also have on the isobars azeotropic mixtures composed of the compound and one of the components. This was observed in the systems we investigated: diethylamine - phenylisothiocyanate and ethylaniline - phenylisothiocyanate. The formation of an azeotrope with a minimum in the first (Fig. 3) and a maximum boiling point in the second system indicated the stability of the thiourea formed and its existence as an individual compound at the boiling point. As one would expect, the ordinates of the singular points on the boiling point isobar are not displaced with a change in pressure, but on the contrary, the composition of the azeotrope changes.

By leveling the singular points of rational systems and smoothly joining the branches of the boiling point isobars we obtain the corresponding types of isobars of irrational systems. Among irrational systems the formation of a compound most frequently leads to the formation of a minimum on the vapor pressure isobar and a corresponding maximum on the boiling point isobar [10].

In these systems, the composition of the azeotrope (resulting from compound formation) can differ to a large or small extent from the composition of the compound; the location of a maximum on the curve depends on the difference between the boiling points of components.

When a comparatively stable and not highly volatile compound is formed in systems whose components do not differ a lot in their boiling points, then the composition of the azeotropic mixture should be close to that of the compound, and in certain systems, also coincide with it [3]. In these cases one can affirm that the maximum azeotrope represents a chemical compound.

This deduction would be particularly convincing if the composition of the azeotrope showed no displacement with change in pressure and coincided with the extrema on the isotherms of other properties which indicated compound formation in the system.

As examples of such systems we can use:  $H_2O - SO_2$  [11],  $C_6H_5NH_2 - HCl$  [12],  $CH_3COOH - (C_2H_5)_2$  [13], systems including  $BF_3$  [3], and others.

We carried out an ebulliometric study of five irrational systems. The boiling point isobars of the stannic chloride - ethyl acetate systems (at 52 and 100 mm of Hg) consisted of continuous curves with maxima at 35.0 and 36.0 mole% respectively.

In our opinion, these data indicate that a reaction occurred in the system with the formation of compound  $SnCl_4 \cdot 2CH_3COOC_2H_5$ ; this is in agreement with the results obtained from the study of other physical properties.

A system similar to the one investigated is that of  $PCl_3 - C_6H_5CHO$ . Boiling point curves at five different pressures consist of two sections convex towards the composition axis and joined at a clearly defined maximum; the maximum is at 76.0 mole% at 152 mm and 79 mole% of  $C_6H_5CHO$  at 360 mm of Hg. The maximum of boiling point isobars is at a composition close to that of previously obtained extrema on isotherms of other properties [14] and characterizes the formation of the compound  $PCl_3 \cdot 3C_6H_5CHO$  in the system.

The boiling points of chloral - water and chloral - ethyl alcohol systems have been previously investigated in part. The boiling point isobar of the first one at 740 mm [15] (Fig. 4) exhibited no characteristic singularities which might have indicated compound formation in the system. However, boiling point isobars which we obtained at lower pressures consisted of smooth curves with a maximum at approximately 50 mole% of  $CCl_3CHO$ ; it

characterized the formation of the compound  $\text{CCl}_3\text{CHO} \cdot \text{H}_2\text{O}$  ( $\text{CCl}_3\text{CHO} \cdot \text{C}_2\text{H}_5\text{OH}$ ) in the other system). There is some data indicating that the above-mentioned compounds exist in the vapor phase [16].

As a result of the investigation carried out we have shown that the boiling point and vapor composition measurements agree with the data on other physical properties and actually supplement them. The data enabled us to establish the existence of interactions in the liquid and vapor phases of the systems and to characterize the stability of the formed compounds under conditions at the boiling points.

All this leads us to the conclusion that ebullioscopic measurements can provide an effective method in the physicochemical analysis of liquid systems.

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# CHROMATOGRAPHIC ANALYSIS OF C<sub>5</sub> HYDROCARBON MIXTURES

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N. M. Turkel'taub

When isopentane is dehydrogenated to isoamylene and isoprene, a multicomponent mixture of hydrocarbons is formed which is essentially composed of C<sub>5</sub> saturated and unsaturated hydrocarbons. According to the literature and our own data [1-4], the investigations on such mixtures were carried out by the use of complicated and tedious physical and chemical analytical methods. Therefore, the purpose of this work was to work out a fast and sufficiently simple method of quantitatively analysing isopentane - isoprene - isoamylene mixtures.

It is known that chromatographic methods of analysis are the fastest, and many investigators make use of various applications of chromatography in separating gaseous and liquid hydrocarbons. Among the possible variations of chromatographic analysis the widest success was achieved by partition chromatography [5] and thermal chromatography [6]. In the present investigation a combination of these two methods was successfully applied to the analysis of C<sub>5</sub> hydrocarbon fractions. The method was worked out on pure individual hydrocarbons and on their artificial mixtures. A Universal Chromothermograph [7] was used for the analysis. Both thermal chromatography and gas - liquid partition chromatography take place in this apparatus. As adsorbents we used aluminum oxide and diatomite impregnated with dibutyl phthalate (25% by weight of adsorbent). The movable temperature gradient, produced with the help of our electric heater, was 2° per 1 cm when the temperature distribution down the heater length was from 20 to 100°. The temperature of the column filled with diatomite was maintained constant within 1°. As carrier gas we used air which was purified to remove water vapor, acid and combustible gases. Its linear velocity was measured on a rheometer and was constant in individual experiments within the range of 120-200 cm/min.

TABLE 1  
Analysis of Artificial Mixtures

Mixt. No.	Composition	Used	Found	Error, abs. %	Mixt. No.	Composition	Used	Found	Error, abs. %
		Wt. %					Wt. %		
4	Isopentane	54.1	53.7	- 0.7	12	Isopentane	83.9	85.8	+ 1.9
	2-Methylbutene-2	45.0	46.3	+ 0.7		3--Methylbutene-1	16.1	14.2	- 1.9
7	Isopentane	83.7	83.6	- 0.1	14	Isopentane	81.2	80.5	- 0.7
	n-Pentane	16.3	16.4	+ 0.1		Pentane-2	18.8	19.5	+ 0.7
8	Isopentane	35.0	36.8	+ 1.8	16	Isoprene	50.1	48.9	- 1.2
	n-Pentane	11.5	11.8	+ 0.3		Trans-piperilene	49.9	51.1	+ 1.2
	2-Methylbutene-2	35.0	32.7	- 2.3	25	Isopentane	34.7	34.3	- 0.4
	2-Methylbutene-1	18.5	18.7	+ 0.2		3-Methylbutene-1	11.4	11.4	0.0
10	Isopentane	79.1	80.5	+ 1.4		2-Methylbutene-1	13.4	13.5	+ 0.1
	2-Methylbutene	20.9	19.5	- 1.4		2-Methylbutene-2	25.5	28.1	+ 2.6
				Isoprene		7.2	5.6	- 1.6	
				Trans-piperilene		7.8	7.1	- 0.7	

Note. The area under the outgoing-gas curves was measured with a PP-2K planimeter.

### Analysis of Ten-component Artificial Mixture No. 18

The figure displays four gas chromatograms, each showing detector response versus time (Xmin). The chromatograms are arranged in a 2x2 grid. The x-axis for the left column plots ranges from 120 to 40 minutes, and for the right column plots from 80 to 20 minutes. The y-axis is labeled 'EPP-09 Readings'.

**Top Left Chromatogram:**

- Peaks labeled: Cis-piperlene, Trans-piperlene, Isoprene, 2-Methylbutene-2, Pentene-2, 2-Methylbutene-1, Pentene-1, n-Pentane, Isopentane, 3-methylbutene-1.
- Xmin scale: 120, 100, 80, 60, 40.

**Top Right Chromatogram:**

- Peaks labeled: 2-Methylbutene-2, 2-Methylbutene-1, Pentene-2, 2-Methylbutene-1, Pentene-1, n-Pentane, Isopentane, 3-methylbutene-1.
- Xmin scale: 80, 60, 40, 20.

**Bottom Left Chromatogram:**

- Peaks labeled: Isoprene, 2-Methylbutene-2, Pentene-2, 2-Methylbutene-1, Pentene-1, n-Pentane, Isopentane, 3-methylbutene-1, Cis-butene-2, Trans-butene-2, Isobutene + butene-1, Butane, Isobutane, Propene, Propane.
- Xmin scale: 120, 100, 80, 60, 40.

**Bottom Right Chromatogram:**

- Peaks labeled: 2-Methylbutene-2, 2-Methylbutene-1, Pentene-2, 2-Methylbutene-1, Pentene-1, n-Pentane, Isopentane, 3-methylbutene-1, Cis-butene-2, Trans-butene-2, Butane, Isobutane.
- Xmin scale: 80, 60, 40, 20.

The concentrations of components in the mixture beyond the absorbent layer were determined with an instrument which was basically designed to measure thermal conductivity of the gas; the presence of very small amounts of admixtures was estimated from the heat of combustion of components in the mixture. Instrument



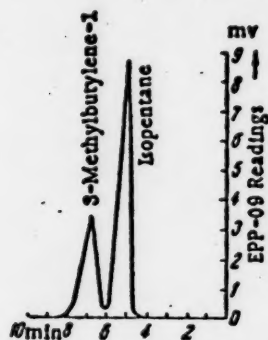


Fig. 2. Chromatogram of a binary isopentane + 3-methylbutene-1 mixture (mixture No. 12).

and 3-methylbutene-1, all the hydrocarbons were clearly resolved. The above-mentioned binary hydrocarbon mixture was separately resolved on aluminum oxide by the use of thermal chromatography (Fig. 2). It is also evident from the analysis of mixture No. 25 (Table 1) that isopentane and 3-methylbutene-1, when both are present in a complex mixture, were determined with sufficient accuracy. Tabulated data on the analysis of artificial mixtures indicate a satisfactory degree of accuracy in the results.

Interpretation of the outgoing-gas curve is an important element in the chromatographic analysis of hydrocarbon mixtures. Since the contents of components in a mixture is determined from the measured areas on the outgoing-gas curve, one has recourse to different methods of measuring areas. For example, one may replace the determination of area by the measurement of concentration at the maximum on the outgoing-gas curve ( $C_{\max}$ ), assuming that  $C_{\max}$  is proportional to the measured area [8]. In this method, however, it is necessary to maintain the reaction conditions very strictly and to calibrate the apparatus for each component of the mixture. Occasionally, in order to measure the area rapidly [9] one may compute it by multiplying the peak height by the band width at half-maximum,  $C = 0.5 C_{\max}$ . Such an approximation is satisfactory if the components are fully resolved. However, in practice it can not be used when the resolution index  $K < 1/2$  [10].

One frequently has to encounter incomplete separation of components when carrying out a chromatographic analysis of hydrocarbon mixtures. Therefore, here we propose a method of calculating the composition of a mixture; the method is based on the assumption that Gaussian distribution is applicable to a linear adsorption isotherm [11]. Then the area  $q$ , corresponding to a given amount of component in the mixture, will in general be determined by the equation

$$q = K_{\theta} C_{\max} \mu_{\theta} \quad (1)$$

where  $K_{\theta}$  = proportionality constant, and  $\mu_{\theta}$  = band width at a given curve point corresponding to a specific ratio  $\theta = C/C_{\max}$ . When  $\theta = 0.5, 0.75$ , and  $0.9$ , constant  $K_{\theta}$ , as calculations have shown, equals 1.065, 1.66, and 2.73, respectively. Depending on how well the components of a mixture are resolved, in computing the area of the outgoing-gas curve one has to choose one of the three  $K_{\theta}$  values and a corresponding  $\mu_{\theta}$ .

To test the proposed method of computing mixture contents we computed the areas by different methods. Such calculations were carried out for the ten-component artificial mixture No. 18 (Table 2). From the listed calculations it is evident that the values computed from Equation (1) with different  $K_{\theta}$  give a satisfactory agreement with each other, as well as with the data obtained planimetrically and the exact concentrations of prepared mixtures. We reached the same conclusion after working on about 30 outgoing-gas curves for the catalytic dehydrogenation products of isopentane and light aviation-benzene fractions.

\*A.I. Karymova and P. S. Pavlova participated in this work.

readings were automatically recorded on 10 mv range EPP-09 potentiometer. An analysis took about 2 hours. We used for the analysis from 5 to 15 ml of an air-hydrocarbon mixture prepared beforehand from the investigated samples. The order and rate of separation were determined on individual hydrocarbon components or by the analysis of artificial mixtures. Since air was used as the carrier gas, calibration curves were used in calculating the composition of mixtures. The contents of each component in the mixture were calculated from the fraction of the total curve area contained under its peak on the outgoing-gas curve.

The experimental results\* obtained from the analysis of artificial mixtures are presented in Tables 1 and 2, and in Fig. 1a we have shown the separation of a complex ten-component artificial mixture of  $C_5$  hydrocarbons (mixture No. 18). One can see from the chromatogram that, with the exception of isopentane



Figs. 1a and b illustrate the applicability of chromatography to the investigation of hydrocarbon catalytic conversion products (dehydrogenation of isopentane) and to the study of composition of light aviation-benzene fractions. These data show the ratios between the principal mixture components and admixtures, which is very important in the study of catalytic processes and in helping solve the problem of how to best utilize petroleum fractions.

Using the analysis of the gaseous aviation-benzene fraction (20-39°) from the catalytic cracking (Fig. 1b) as an example, we can resolve its composition in detail and determine impurities in the principal material - isopentane. Beside isopentane (88.6 wt. %) the fraction contained three hydrocarbons (isobutane, 3-methylbutene-1, and pentene-1) in amounts up to 1% by wt., and from 1 to 2% by weight of seven other hydrocarbons (n-butane, cis- and trans-butene-2, n-pentane, 2-methylbutene-1, pentene-2, and 2-methylbutene-2).

The Universal Instrument can also be used for the determination of hydrocarbon purity. Thus, isopentane isolated from a natural-gas condensate contained as impurities, 1% by weight of n-butane and 0.4% by wt. of n-pentane. Therefore, in the present investigation, by using chromatographic methods, we worked out a technique for the quantitative analysis of complex  $C_5$  hydrocarbon mixtures of various structures with lighter hydrocarbons as impurities.

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\*Original Russian pagination. See C. B. Translation.

## CHLORINATED POLYPROPYLENES

K. S. Minsker and V. S. Etlis

(Presented by Academician V. A. Kargin May 16, 1958)

As Natta and co-workers have noted [1], chlorine reacts with crystalline polypropylene to form white, brittle (degree of brittleness depends on the chlorine contents) materials which slowly lose chlorine at 80-100°. If chlorine content is high, a complete disruption of structure takes place.

The conditions of synthesis and properties of products with respect to the chlorine contents in the polymer were not described.

In connection with this it seemed interesting to carry out a more detailed investigation of polypropylene chlorination; two types of polymer were prepared, one catalyzed by  $Al(C_2H_5)_3 + TiCl_4$  (I) (33% amorphous fraction, 45% isotactic fraction), the other by  $Al(C_2H_5)_3 + TiCl_3$  (II) (7% amorphous fraction, 85% isotactic fraction).

Chlorination was carried out in a chlorobenzene medium in the presence or absence of initiators (radical donors).

We would use 45-50 g of polypropylene per liter of chlorobenzene and begin to bubble gaseous chlorine at 45° at the rate of 40-45 g/hour. After that the temperature in the reactor was raised to 75-80° and maintained at level during the whole process. If the reaction was carried out in the presence of initiators, then in the course of reaction we added every hour 0.28 g of 2,2'-azo-bis-isobutyronitrile or any other compound which would readily generate radicals at the experimental temperature.

We separated the polymer from the solvent by either precipitating it with alcohol (methanol, for example) or by steam-distilling the solvent.

In Fig. 1 we have plotted chlorination kinetics of polypropylenes (I) and (II) in the presence of initiators (Curves 2 and 1 respectively), or in their absence (Curve 3). Use of initiators increased the reaction rate, especially that of the polypropylene with a higher isotactic fraction content. We were unable to attain the composition  $(C_3H_2Cl)_n$  under these conditions, even with prolonged chlorination in the presence of an initiator.

When chlorine is introduced into the polymer, pronounced changes occur: at first (10-15.0% Cl) the resulting material crumbles, then it passes through a fibrous stage (40-50% Cl, corresponding to a polymer of structure  $(C_3H_2Cl)_n$ ), and finally a noncombustible powdery material is formed again. As the chlorine content in the polypropylene is raised, the solubility of the material increases, viscosity decreases (especially in the presence of an initiator, Fig. 2), and density increases (Fig. 3, 2). All the prepared samples turned out to be amorphous, as electron-diffraction studies indicated.

A lowering in the specific viscosities of polypropylenes (I) and (II) indicates a rupture of C-C bonds in the polymer chain (chain disintegration). Increased density of chlorinated polypropylenes permits the assumption that, after 30-35% of chlorine is introduced, both polymers assume the same or similar structures, whereas the general structure of original polymers actually differed in their contents of amorphous and isotactic fractions, which was reflected in the densities of starting materials (density of polymer (I) was  $0.89 \pm 0.005$ , while density of (II) was  $0.92 \pm 0.005$ ).

Interesting results were obtained on the softening temperatures of chlorinated polypropylenes as a function of chlorine contents. At low chlorine contents the softening temperatures of samples decreased, then, as more

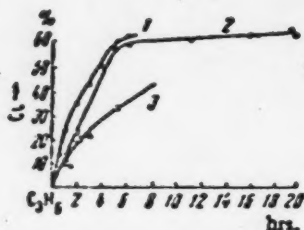


Fig. 1. Polypropylene chlorination kinetics.

1) Polymer (II); 2) polymer (I) in the presence of 2,2'-azo-bis-isobutyronitrile; 3) (I) without initiator.

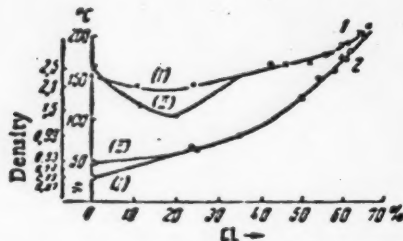


Fig. 3. Change in the melting point (1) and density of samples (2) as a function of chlorine contents.

chlorine was introduced into the polymer molecule, it started increasing, and at 65-66% chlorine contents it went up to 200° and above (Fig. 3, 1). A polymer containing 15-20% of chlorine, i. e., one which had less than one chlorine per  $\text{CH}_2$  side group, had a minimum melting point.

If we assume that the chlorines replace only the hydrogens in  $\text{CH}_2$  side groups, then it is obvious that decreased melting point may be attributed to a disruption in the high-molecular polymer structure, resulting from an interaction between slightly positive  $\text{CH}_2$  and negative  $\text{CH}_2\text{Cl}$  groups. When the number of  $\text{CH}_2\text{Cl}$  groups exceeds 1/3-1/2 of all the available  $\text{CH}_2$  side groups, then the polymer evidently may again become more regular, obviously due to a mutual re-

pulsion between similarly charged  $\text{CH}_2\text{Cl}$  groups, which leads to an increase in the melting point of the polymer. When the polymer has exclusively  $\text{CH}_2\text{Cl}$  groups, then its melting point assumes the value of the isotactic product (165-175°). When  $\text{CH}_2$  groups are substituted with two chlorines, the polypropylene acquires a sharp melting point, of the order of 200°.

Further substitution by chlorine proceeds much slower, while the softening temperature increases even more and the polymer itself becomes more and more brittle.

Similarity of phenomena observed in the chlorination of isotactic and atactic polymers can also be explained by the possibility that a hydrogen on the tertiary carbon atom is replaced with chlorine, which disturbs the regular spatial orientation of substituents in the macromolecule and disrupts the crystal structure.

Similar results were also obtained when the thermomechanical properties were investigated on a Kargin balance (Fig. 4). Thermomechanical data provided fairly precise melting points of samples.

Chlorinated polypropylenes with more than 45% of chlorine do not have a temperature range of high elasticity but pass directly from a glassy state into one of viscous fluidity.

Like all chlorine-containing polymers, chlorinated samples of (I) and (II) have a tendency to give off  $\text{HCl}$  readily. Thus, investigated samples with an average chlorine content of about 60% (polymer of  $(\text{C}_3\text{H}_4\text{Cl}_2)_n$  structure) readily split out  $\text{HCl}$  at 108-123° (tested with Congo red). Usual stabilizers used to stabilize polyvinyl chloride produced a pronounced increase in the decomposition temperature of chlorinated polypropylenes.

Thus, addition of 4% of calcium stearate would raise the decomposition temperature to 171-173°, soybean oil epoxide to 174°, lead silicate to 188°.

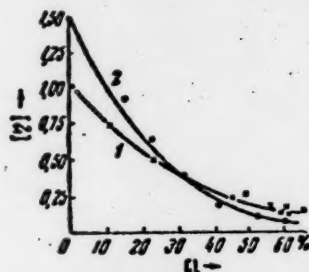


Fig. 2. Polymer density as a function of chlorine contents.

1) Polymer (I); 2) polymer (II).

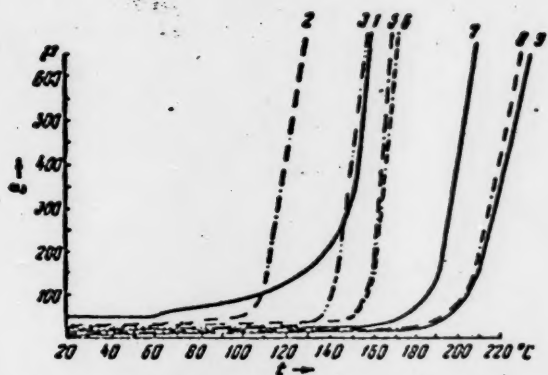


Fig. 4. Thermomechanical curves of chlorinated polypropylene (by immersion of a plunger 3 mm in diameter and 740 g/cm<sup>2</sup> load,  $\tau = 10$  sec). 1) Initial polymer; 2) 23.0% Cl; 3) 36.5% Cl; 4) 49.2% Cl; 5) 56.5% Cl; 6) 59.0% Cl; 7) 61% Cl; 8) 64.0% Cl; 9) 65.4% Cl.

One should note that stabilized samples when solidified, again had a low decomposition temperature (of the order of 118-130°).

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# SYNTHESIS AND RESOLUTION OF CIS- AND TRANS- 1,2-DIALKYL-CYCLOPENTANES

A. F. Plate, A. A. Mel'nikov, R. A. Zelenko, and N. I. Lykova

(Presented by Academician B. A. Kazanskii, July 14, 1958)

The chemical composition of gasoline has been investigated and found to include in majority of cases appreciable quantities of cyclopentanes. As far as the ligroin - petroleum fraction is concerned, the nature of hydrocarbons contained in it has not been studied sufficiently, while the structure of cyclopentane hydrocarbons has hardly been investigated at all. However, in recent years the problem of ligroin and kerosene hydrocarbon composition has become particularly acute due to the importance these fractions assumed as fuels for jet engines and Diesel motors. This type of investigation is considerably limited by the lack of standard hydrocarbons which are necessary, in particular, for a successful application of spectral analytical techniques.

TABLE 1

Physical Constants of Synthesized Unsaturated Hydrocarbons

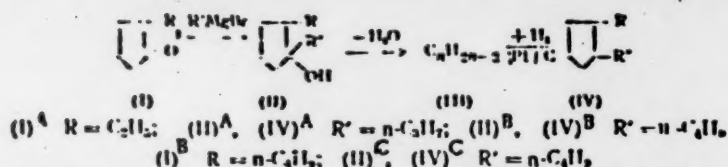
Compd. No.	Hydrocarbon	B. p.	$n_D^{20}$	$d_4^{20}$	MR <sub>D</sub>		% Yield of theor.
					Found	Calculated	
1	C <sub>10</sub> H <sub>18</sub>	60-60.5°/15 mm	1.4532	0.8157	45.82	45.71	65.3
2	C <sub>11</sub> H <sub>20</sub>	60-60.7°/5 mm	1.4545	0.8158	50.59	50.33	78.7
3	C <sub>12</sub> H <sub>22</sub>	70.5-71.0°/3 mm	1.4570	0.8244	59.57	59.57	77.7

Remarks. I. All hydrocarbons become vitreous when cooled. II. For No. 1. Found %: C, 86.32; 86.14; H, 12.86; 12.97. C<sub>10</sub>H<sub>18</sub>. Calculated %: C, 86.88; H, 13.12. For No. 2. Found %: C, 86.90; 87.06; H, 13.07; 13.14. C<sub>11</sub>H<sub>20</sub>. Calculated %: C, 86.76; H, 13.24. For No. 3. Found %: C, 86.07; 86.36; H, 13.48; 13.50. C<sub>12</sub>H<sub>22</sub>. Calculated %: C, 86.58; H, 13.42.

Our goal was to synthesize 1,2-dialkylcyclopentanes C<sub>10</sub>H<sub>18</sub>-C<sub>12</sub>H<sub>22</sub> and to resolve them into cis- and trans-isomers.

When the compounds contained in gasolines (from a series of domestic petroleum samples) were investigated, it was shown that mono-, di-, and tri-substituted cyclopentane hydrocarbons were present [1,2]. It was also shown that the 1,2-dimethylcyclopentane and 1-methyl-2-ethylcyclopentane contained in gasolines consisted of a mixture of trans- and cis-isomer, with the first one in considerable excess (61.3-87.3% of stereoisomers) [1,3]. Up to the present time only a small number of 1,2-dialkylcyclopentanes have been synthesized. Individual cis and trans-isomers of the following compounds have been isolated: 1,2-dimethylcyclopentane, 1-methyl-2-ethylcyclopentane [4], 1,2-diethylcyclopentane [5], 1-methyl-2-n-propylcyclopentane [6], and 1-methyl-2-n-butylcyclopentane [7]. Besides, there are indications in the literature that the following have been synthesized: 1,2-diheptylcyclopentane, 1,2-dioctylcyclopentane, 1-butyl-2-dodecylcyclopentane, 1-hexyl-2-decylcyclopentane, and 1-heptyl-2-nonylcyclopentane; however, this work [8] did not mention the spatial configuration of these hydrocarbons or the structure of alkyl substituents.

1-Ethyl-2-n-propylcyclopentane, 1-ethyl-2-n-butylcyclopentane, and 1,2-di-n-butylcyclopentane were prepared in this work according to the scheme shown below,



From ketones (I) (purified by recrystallization as semicarbazones) and alkylmagnesium halides we prepared the corresponding tertiary alcohols (II) in a 50-72% yield (of theoretical); these alcohols were a mixture of cis- and trans-isomers and therefore distilled over a wide temperature range. Dehydration of alcohols in the presence of iodine (1,2-di-n-butylcyclopentanol-1) or a saturated solution of oxalic acid (1-ethyl-2-n-propylcyclopentanol-2, and 1-ethyl-2-n-butylcyclopentanol-2) gave a 65-78% (of theoretical) yield of unsaturated hydrocarbons (III). Their constants are listed in Table 1.

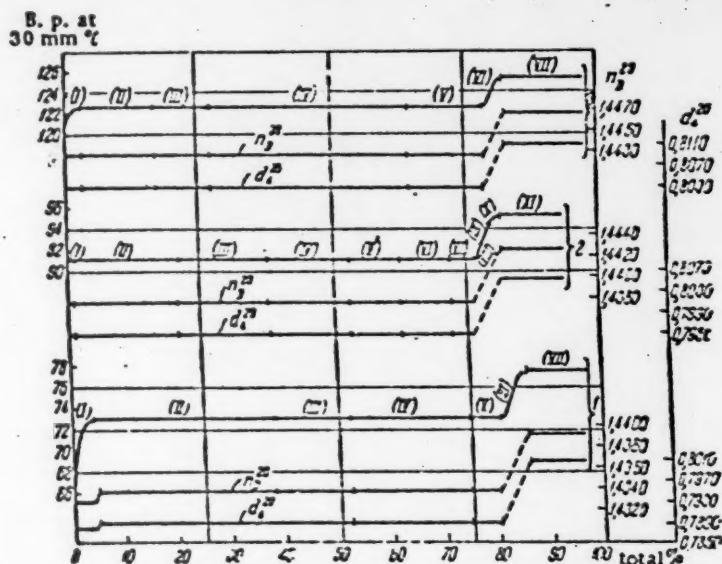
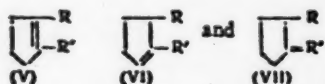


Fig. 1. Fractionation curves of hydrocarbons and physical constants of fractions. 1) 1-Ethyl-2-n-propylcyclopentane; 2) 1-ethyl-2-n-butylcyclopentane; 3) 1,2-di-n-butylcyclopentane.

Since dehydration of alcohols (II) may proceed in three directions, then compound (III) can be a mixture of three isomers:



On the basis of Raman spectra one can make a good guess concerning the composition of these mixtures.\* For each of the two unsaturated hydrocarbon mixtures prepared from 1-ethyl-2-n-butylcyclopentanol-2 and 1,2-di-n-butylcyclopentanol-1 we detected two lines in the region of double bond vibrational frequencies: 1652(5) and 1676(10) cm<sup>-1</sup> and corresponding ones at 1652(4) and 1673(8) cm<sup>-1</sup>. This indicates that the investigated unsaturated hydrocarbons were a mixture of isomers with double bonds in different positions. If these spectra were compared with those of 1-alkylcyclopentenes-1 and 1,2-dialkylcyclopentenes [9], then one could assume that the mixture obtained from 1-ethyl-2-n-butylcyclopentanol-2 consisted of 70-85% 1-ethyl-2-n-butylcyclopentene-1 and 15-30% 1-ethyl-2-n-butylcyclopentene-2, possibly with an admixture of 1-ethyl-2-n-butyldienecyclopentene-1.

\*We take this opportunity to express our gratitude to V. T. Aleksanian and Kh. E. Sterin for carrying out the spectral analysis in the Spec. Comm. Lab. Acad. Sci. USSR.

TABLE 2

Physical Constants of Cis and Trans-Isomers of Synthesized Hydrocarbons

Compd. No.	Hydrocarbon	Configura- tion	B. p., °C		$n_D^{20}$	$n_D^{25}$	$d_4^{20}$	$d_4^{25}$	MR <sup>20</sup> <sub>D</sub>		Isomer Yield, % of total HIC
			at 30 mm	Conver- ted to 760 mm*					Found	Calc.	
1a	1-Ethyl-2-n-propylcyclopentane	Trans	72,9	170,8	1,4337	1,4317	0,7898	0,7857	46,22		82,7
b	Ditto	Cis	77,4	176,4	1,4391	1,4371	0,8008	0,7965	46,08	46,18	12,3
2a	1-Ethyl-2-n-butylcyclopentane	Trans	91,0	193,0	1,4376	1,4354	0,7950	0,7913	50,90		81,0
b	Ditto	Cis	95,3	198,1	1,4426	1,4404	0,8054	0,8017	50,75	50,80	13,8
3a	1,2-di-n-butylcyclopentane	Trans	122,6	231,1	1,4427	1,4409	0,8028	0,7993	60,18		80,9
b	Ditto	Cis	125,4	234,5	1,4467	1,4449	0,8111	0,8077	60,03	60,08	15,6

\* Conversion was done with the help of tables [11].

Remarks. I. Trans-1,2-di-n-butylcyclopentane (No. 3a) had a m. p. -62.7°; melting point recalculated to 100% purity -62.55°, purity 99.75%. All the remaining hydrocarbons, and also cis-1,2-di-n-butylcyclopentane turn vitreous on cooling. II. For No. 1. Found %: (No. 1a) C, 85.53, 85.53; H, 14.20, 14.18; (No. 1b) C, 85.52, 85.56; H, 14.23, 14.14.  $C_{15}H_{28}$ . Calculated %: C, 85.63; H, 14.37. For No. 2. Found %: (No. 2a) C, 85.58, 85.54; H, 14.30, 14.30; (No. 2b) C, 85.91, 85.86; H, 14.31, 14.40.  $C_{17}H_{32}$ . Calculated %: C, 85.63; H, 14.37. For No. 3. Found %: (No. 3a) C, 85.81, 85.73; H, 14.16; 14.18; (No. 3b) C, 85.54, 85.61; H, 14.28, 14.36.  $C_{17}H_{32}$ . Calculated %: C, 85.63; H, 14.37.

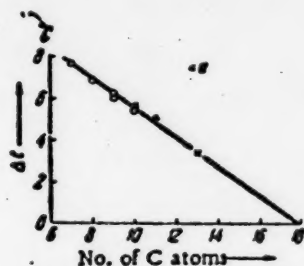


Fig. 2.  $\Delta t_b$  of 1,2-dialkylcyclopentanes as a function of the number of carbon atoms in the molecule.  $\Delta$  = Hydrocarbons synthesized in this work.

clopentane. The mixture obtained from 1,2-n-butylcyclopentanol-1 was composed of 60-80% 1,2-di-n-butylcyclopentene-1 and 20-40% 1,2-di-n-butylcyclopentene-2, possibly with an admixture of 1-n-butyl-2-n-butylidenecyclopentane. Thus, in both mixtures structure (V) predominated. Dehydration products of 1-ethyl-2-n-propylcyclopentanol-2 were not analyzed spectrally.

The boiling points of unsaturated hydrocarbons obtained from the dehydration of the same alcohol were very close, and consequently, the compounds were not separated but were hydrogenated together in the mixture. Each such mixture should yield just one kind of saturated hydrocarbon on hydrogenation. Hydrogenation was carried out at room temperature in an alcoholic solution in the presence of platinumized carbon (5% Pt) activated with palladium chloride

[10]. The synthesized 1-ethyl-2-n-propylcyclopentane, 1-ethyl-2-n-butylcyclopentane and 1,2-di-n-butylcyclopentane were first purified through chromatographic adsorption on silica gel, then separated into cis- and trans-isomers by vacuum distillation on an efficient 80 T. P. column with metallic packing. Fractionation curves and changes in the physical constants of fractions are shown in Fig. 1. Physical constants of synthesized hydrocarbons are listed in Table 2.

\* We take this opportunity to express our gratitude to V. T. Aleksanjan and Kh. E. Sterin for carrying out the spectra analysis in the Spec. Comm. Lab. Acad. Sci. USSR.

In accordance with the von Auwers-Skita rule we assigned *cis* configuration to stereoisomers with a higher relative boiling point, refractive index, and density, and a lower molar refraction. In this work the *cis*- and *trans*-isomers were obtained in the ratios of 1:5.2 to 1:6.7. The crystallization point and degree of purity (99.75%) of *trans*-1,2-di-*n*-butylcyclopentane had been determined [12]. The crystallization points of *cis*-1,2-di-*n*-butylcyclopentane, *cis*- and *trans*-isomers of 1-ethyl-2-*n*-butylcyclopentane and 1-ethyl-2-*n*-propylcyclopentane could not be determined because these hydrocarbons became vitreous when cooled.

As may be seen from Fig. 2, our data support and supplement the results of B. A. Kazanskii, A. L. Liberman, and co-workers [13], who showed that the differences in the boiling points of all the so-far-known stereoisomeric dialkylcycloalkanes are linearly dependent on the number of carbon atoms in the molecule. The boiling point differences among the stereoisomers synthesized by us fit well into this function; consequently, the von Auwers-Skita rule should be applicable to  $C_{13}H_{26}$ - $C_{15}H_{28}$  1,2-dialkylcyclopentanes. Therefore, the configurations which we assigned to the stereoisomers prepared in this work can be considered correct.

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\* In Russian.

\*\* As in original - Publisher's note.

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